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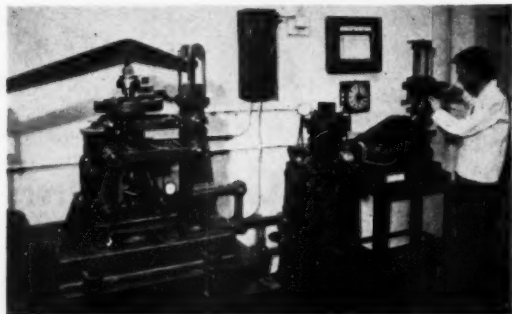
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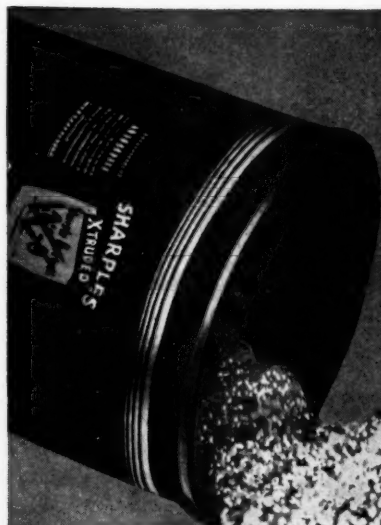


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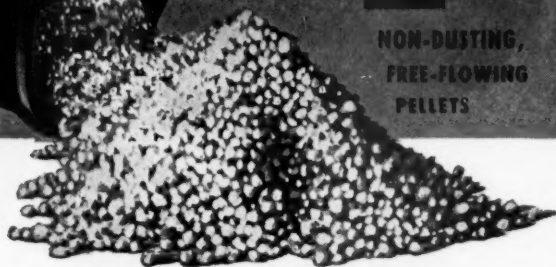
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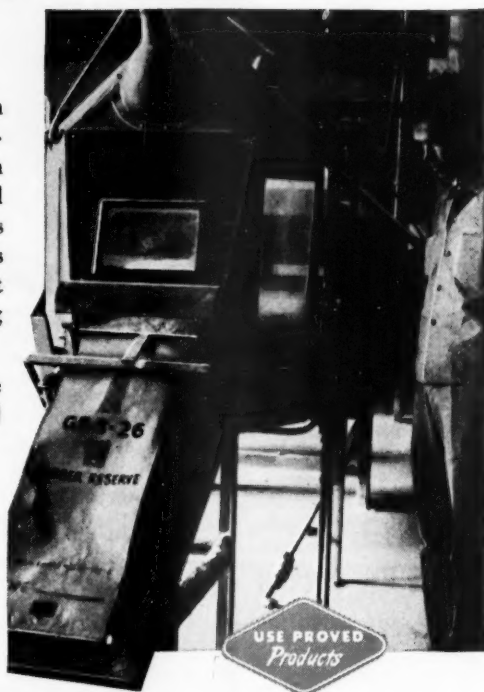
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RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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Chairman . . . NEIL MCINTIRE (Oliver Tire & Rubber Co., Emeryville). *Vice-Chairman* . . . J. H. HOLLISTER (Mare Island Naval Shipyard, Vallejo). *Secretary* . . . J. A. SANFORD (American Rubber Manufacturing Co., Oakland). *Treasurer* . . . W. H. DEIS (Goodyear Rubber Co., San Francisco). (Terms expire December 31, 1952.)

PHILADELPHIA

Chairman . . . T. W. ELKIN (Armstrong Cork Co., Lancaster, Pa.). *Vice-Chairman* . . . G. J. WYROUGH (R. E. Carroll, Inc., Trenton, N. J.). *Secretary-Treasurer* . . . ANTHONY DI MAGGIO (Firestone Tire & Rubber Co., Pottstown, Pa.). (Terms expire at meeting in January 1953.)

RHODE ISLAND

Chairman . . . C. L. KINGSFORD (Daval Rubber Co., Providence). *Vice-Chairman* . . . R. G. VOLKMAN (U. S. Rubber Co., Providence). *Secretary-Treasurer* . . . F. B. BURGER (Kleistone Rubber Co., Warren). (Terms expire at fall meeting 1952.)

SOUTHERN OHIO

Chairman . . . JACK FELDMAN (Inland Manufacturing Division, General Motors Corp., Dayton). *Vice-Chairman* . . . GEORGE LANG (Johnson Rubber Co., Middlefield). *Secretary* . . . R. J. HOSKIN (Inland Manufacturing Division General Motors Corp., Dayton). *Treasurer* . . . DAYLE BUCHANAN (Inland Manufacturing Division, General Motors Corp., Dayton). (Terms expire December 31, 1952.)

WASHINGTON, D. C.

Chairman . . . T. R. SCANLAN (Gates Rubber Co., Washington). *Vice-Chairman* . . . NORMAN BEKKEDAHL (National Bureau of Standards, Washington). *Secretary* . . . GERALD REINSMITH (Army Office of the Chief of Ordinance Washington). *Treasurer* . . . PHILIP MITTON (Army Engineering Research and Development Laboratory, Washington). *Recording Secretary* . . . ETHEL LEVENE (Navy Bureau of Ships, Washington). (Terms expire October 1952.)

NEW BOOKS AND OTHER PUBLICATIONS

COPOLYMERIZATION. By T. Alfrey, Jr., J. J. Bohrer, and H. Mark. London and New York, Interscience Publishers, Vol. VIII in High Polymer Series, 1952, pp. 269. 54s. Od. post free from London.—Copolymers had been developed commercially for many years before, in 1929, a systematic theoretical study of their structure was commenced, and this volume is claimed to be the first book on the physical chemistry of copolymerization in general terms. The development of plastics and synthetic rubbers has passed from the stage of accidental discovery to that of designing materials with predetermined characteristics. A study of this book is recommended to every worker in this field because almost every aspect, from the structure of the monomers to the influence of the reaction conditions, is considered in detail.

The treatment of reaction kinetics and the thermodynamic functions is mathematical, but every step is explained in the text. Factors such as resonance stabilization, steric hindrance, and polar substituents in monomer systems are analyzed, and the influence of the reaction medium is traced. The structure and configuration of the products is the subject of a rather short chapter, and cross-linking (termed "vulcanization" in the text), is treated statistically. A separate chapter is devoted to a consideration of diene copolymerization, and related problems, such as 1,2- or 1,4- addition and the cross-linking of residual double bonds, are discussed qualitatively.

A free radical mechanism is assumed except in one chapter which somewhat briefly deals with the ionic initiation of copolymerization by the Friedel Crafts types of catalyst. In view of the increasing importance of this kind of copolymerization, e.g., in the production of Butyl rubber, the comparative dearth of information on this subject is unfortunate. The technologist's attention will be directed to the last chapter, which gives a summary of the influence of the monomer units on the properties of the products.

It should be emphasized that the work is concerned with the general case rather than particular systems, but the bibliographies at the end of each chapter refer the reader to literature on practical applications, and tables of data throughout the text give constants for every common copolymerizable compound. There is an adequate subject index. [From the *India-Rubber Journal*.]

EXTRUSION OF PLASTICS, RUBBER, AND METALS. By Herbert R. Simonds, Archie J. Weith, and William Schack. Published by Reinhold Publishing Corp., 330 West 42nd St., New York 17, N. Y. 6 × 9 in. 454 pp. \$10.00—Although reference to the extrusion process in various manufacturing operations appears in numerous books and in the technical literature of various fields, the literature has been lacking a single volume devoted to this important and rapidly growing process. The book under review bridges the gap in the literature by providing for the first time a complete coverage of extrusion as an important processing operation. Although the emphasis is on plastics, many of the principles described are applicable to other materials, and descriptions of the processes of extrusion of rubber, metals, ceramics, graphite, and other materials are included. Special attention is paid by the authors to recent advances in the field, and all descriptions of extrusion methods have been geared to the nature and actual operation of factory equipment.

The book includes a 15-page chapter on the "Extrusion of Rubber," covering such subjects as the various types of rubber and their special properties, required conditioning of the rubber before extrusion, processing steps, production of inner tubes, and a section devoted to the new silicone rubbers. A comparison of the properties of various rubbers is given in tabular form, and a table outlining the chemical and physical properties of both the G-E and Dow Corning silicone rubbers is included. Cost figures given in the text add to the value of the chapter.

The book is divided into two parts, and has 18 chapters in all. An appendix includes a glossary, manufacturers of extruded products and extrusion equipment, and tables and conversion factors. There is also a general index. [From *The Rubber Age* of New York.]

MACHINERY AND EQUIPMENT FOR RUBBER AND PLASTICS. VOL. I—PRIMARY MACHINERY AND EQUIPMENT. Compiled by R. G. Seaman and A. M. Merrill. Published by India Rubber World, 386 Fourth Ave., New York 16, N. Y. 6 X 9 in. 804 pp. \$15.00 domestic; \$16.00 foreign.—As indicated in its preface, this book has been compiled "for those men of the rubber and the plastics industries who are responsible in one way or another for the processing of the various raw materials used by these industries into many thousands of finished products daily." To this end, the book presents comprehensive engineering information on the primary machines and equipment used by the rubber and plastics industries. A second volume, now in preparation, will cover auxiliary equipment and accessories.

The current volume, compiled by the editors of *The India Rubber World* with the cooperation of an editorial advisory board, covers mills, mixers, calenders, extruders, presses, etc., in 20 separate chapters, each chapter subdivided into sections. Each chapter begins with one or more introductory articles by recognized authorities discussing design trends, construction principles, and applications. This is followed by classified descriptions of specific equipment arranged by supplier and based on information furnished by such suppliers. Advertisements from some of the suppliers appear at the end of almost every chapter. Illustrations are liberally used throughout.

The machinery and equipment covered in this first volume include the following: (1) mills; (2) mill accessories; (3) mixers; (4) calenders and accessories; (5) extruders; (6) extruder accessories; (7) compression presses; (8) press accessories; (9) injection presses; (10) molds and mold accessories; (11) web coating and handling equipment; (12) pressure vessels; (13) heaters, dryers and coolers; (14) tire and tube machinery; (15) hose and belting machinery; (16) footwear machinery; (17) wire and cable machinery; (18) sole and heel machinery; (19) latex machinery; (20) special plastics machinery.

Among the contributors of the introductory articles are P. C. Taylor (Ohio Rubber), Julian C. Smith (Cornell), E. H. Johnson (Farrel-Birmingham), A. L. Heston (National Rubber Machinery), H. E. Buecken (National Rubber Machinery), E. R. Coddington (National Rubber Machinery), A. J. de Matteo (Watson-Stillman), H. H. Wydom (Brockton Tool), R. C. Quine (Akron Equipment), Harold P. Lamb (Adamson United), Paul Beebe (Goodyear), L. Cranston (U. S. Rubber), W. E. Glancy (Hood Rubber), R. A. Schatzel (Rome Cable), W. E. Kavenagh (Goodyear), and P. D. Brass (U. S. Rubber).

An appendix includes a list of used and rebuilt machinery dealers, data on accumulators, pumps, and intensifiers, and a complete list of the names and

addresses of the 350 companies whose products are described in the text. A subject index is also included. [From *The Rubber Age* of New York.]

THE FIRESTONE STORY. By Alfred Lief. Whittlesey House, McGraw-Hill Book Co., Inc., 330 W. 42nd St., New York 18, N. Y. Cloth, 6 by 9 inches, 444 pages. Price, \$4.50.—This book presents an interesting and comprehensive history of the first 50 years of The Firestone Tire & Rubber Co. since its inception on August 3, 1900. More properly, the book is a history and tribute to the company's founder, Harvey S. Firestone, whose policies and efforts shaped the company's formative years and the stages of growth and expansion which followed. At the same time the author presents a fascinating review of business conditions and growth and the problems of a competitive economy during the first half of the Twentieth Century.

All aspects of the company's growth and development are described in detail in narrative form. Much of the story deals with the development of tires from the original solid internalwire types to the present low-pressure models, and the effects of tires and highway transportation on the domestic economy and way of life. The different problems encountered with rim standardization, rubber quality, availability, and price considerations, sales and promotional techniques, labor and economic difficulties, and others are all described in relation to the overall view of tire development.

Other company activities are treated in detail in tracing the company's management, technical, productive, and sales growth and development. The story ranges from the beginnings in Akron to the Liberian rubber plantations and the present world-wide structure of the firm, with due attention to the development of employee relations programs, farm service work, and extensions into the field of banking, cotton fabrication, rim manufacture, dealer stores, and the manufacture of plastics, batteries, and other products. [From the *India Rubber World*.]

STATISTICAL DESIGN AND ANALYSIS OF EXPERIMENTS FOR DEVELOPMENT RESEARCH. By Donald S. Villars. William C. Brown Co., 915 Main St., Dubuque, Iowa. Cloth, 5½ by 8½ inches, 472 pages. Price, \$6.50.—Based on courses and lectures given at various universities, this book summarizes the fundamental principles involved in the design of efficient experiments. A journalistic style is employed so that the reader may almost immediately begin applying various analyses to his own data, without having to go any deeper into the subject than he desires. Major emphasis is placed on the techniques of small sample statistical analysis for use in laboratory and development work rather than on large sample analysis applicable to plant or mass-production operation.

Of particular value is a detailed study of replication degeneracy, a design where several different types of treatments are repeated to differing extents. An understanding of the simple principle involved in this design will prevent the beginner from making erroneous "statistical" conclusions. In addition, the author formulates a rational system for determining the correct method of analyzing variance. New and extended tables of variance components are worked out, and a detailed description is given of the technique for applying these components to determine the appropriate error estimate for a legitimate significance test.

Many tables of actual test data and typical calculations are used to illustrate the text. Many of these illustrations are drawn from the author's exten-

sive experience in the rubber industry. While the journalistic approach presents working data early in the book, theoretical considerations are also covered in the later chapters. For the convenience of the beginner, a comprehensive glossary of terms is included, and the book also contains lists of typical problems with their solutions, and both author and subject indexes. [From the *India Rubber World*.]

STANDARDS ON TEXTILE MATERIALS. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 612 pp. \$5.00.—Prepared by Committee D-13 on Textile Materials, the latest edition of this compilation includes, in their most recent form, 88 specifications, methods, and tolerances developed by the Committee. Included for the first time are very comprehensive tentative methods for resistance to abrasion of textile fabrics. Considerable other material on textile testing is included. As usual, there is a convenient table of contents (by subject and A.S.T.M. serial designation) and an index of methods of test. [From *The Rubber Age* of New York.]

METHODS OF MEASURING HUMIDITY AND TESTING HYGROMETERS. NBS Circular 512. By Arnold Wexler and W. G. Brombacher, National Bureau of Standards, United States Department of Commerce. For sale by the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. 20 pages. Price, \$0.15.—This paper reviews methods for measuring moisture vapor content of air and other gases and for producing and controlling atmospheres of known humidity. Various hygrometric techniques are also discussed, with suitable equipment. 157 literature references are included. [From the *India Rubber World*.]

CHEMICAL ENGINEERING CATALOG. Thirty-Sixth Annual Edition, 1951-52. Reinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. Cloth, 8 by 11 inches, 1,797 pages. Price \$20.—This newest member of the series of annual reference catalogs presents information on chemical processing equipment and engineering materials offered by 482 participating companies. Reflecting the continued growth of the chemical industry, this new edition shows an increase of 117 pages over the preceding issue. A new feature is the functional guide to the classified index, wherein all of the existing headings in the regular classified subject index are grouped into 14 broad functional topics. By this means, all related subjects covered in the catalog can be seen at a glance. In addition to the functional guide and classified index, the book contains a firm name index, trade name index, and catalog section. [From the *India Rubber World*.]



DOUGLAS FRANK TWISS 1883-1951

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Among the celebrated names of those who have contributed so much in the last thirty years to rubber technology is that of Douglas Frank Twiss. Born in Birmingham, England, in 1883, he graduated at Birmingham University and received the Doctor of Science degree in 1910. Among other academic qualifications, he was a Bachelor of Science of London University and became a Fellow of the Royal Institute of Chemistry in 1908, on whose Council he served for nine years. He was also one of the pioneer members of the Institution of the Rubber Industry at its inception in 1921, and in 1934 he received the highest honor the Institution awards—the Colwyn Gold Medal—for his outstanding scientific work in rubber technology.

During the long and active part he played in the British rubber industry, he served on various committees of the Research Association of British Rubber Manufacturers and the Institution of the Rubber Industry.

Dr. Twiss's first appointment was as a lecturer in chemistry at the Birmingham College of Technology until 1914, when he joined the Dunlop Rubber Company to form a Chemical Research Department. Within a year he was appointed Chief Chemist, a position he held until his retirement in 1946.

Some idea of his wide and varied interests can be obtained from over seventy scientific publications and two hundred patent specifications bearing his name and sometimes those of his fellow workers. He was also part author of a text book on practical organic chemistry and two volumes on inorganic chemistry dealing with oxygen and sulfur, and he served for many years as Special Editor in rubber and elastomers for British Abstracts.

Although in the early days of his career he was not to know of his subsequent life work for the rubber industry, he was interested in organic sulfur compounds right from the beginning of his career, and from 1907 to 1908 papers were published with T. S. Price on the preparation of organic disulfides by electrolytic reduction of sodium alkylthiosulfate, which showed that in this way pure disulfides uncontaminated by any thiol were readily obtained.

As a development of this work, there were further publications from 1912-1914 on the molecular refractivity of organic sulfur compounds, in which it was found that with sulfur (as in the case of nitrogen), the values depend on its mode of combination and show wide divergence. Values for the thiols, thiocyanates, and disulfides were determined, which showed that much higher molecular refractivity is associated with doubly linked sulfur atoms, as in xanthates and dithiocarbonates.

Between 1914 and 1920, various papers appeared on improved methods and equipment for use in the chemical analysis of rubber and rubber products. Twiss also, during this period, published several papers on the chemistry of vulcanization.

Between 1920 and 1924 a number of important papers were published on the vulcanization of rubber with organic accelerators. The characteristic features of vulcanization using metallic xanthates were investigated by Twiss and Thomas. They showed that the activity of zinc alkylxanthates is greatly influenced by the presence of suitable metallic oxides, such as zinc oxide. Not only did zinc oxide promote the acceleration to a marked degree, but striking improvements in physical properties of the product also resulted. They found that the use of a zinc alkylxanthate enables rapid vulcanization, even at temperatures as low as 78° C. Cadmium alkylxanthates possess similar properties, and cadmium oxide was found to be almost as effective as zinc oxide in promoting the activity of alkylxanthates. Mention had previously been made by Bruni and Romani of zinc ethylxanthate, but Twiss and Thomas were the first to record in the English chemical literature the characteristic features of vulcanization with the aid of metallic xanthates. In work on the dithiocarbamate accelerators, Twiss, Brazier, and Thomas reported on the unusually high tensile strength of the vulcanized products, and showed the necessity for the accompanying presence of zinc oxide for full effectiveness of the accelerators. Twiss carried out experiments on the discontinuity and double inflection in the extensibility curve for a rubber/sulfur mix containing 1 per cent of HMT and 1 per cent of zinc oxide. The abnormality of this curve was essentially restricted to a short ascending portion of the curve, where increasing vulcanization time caused an increase of extensibility. This was thought to be due to an abnormal softening effect on the rubber "which can conveniently, but possibly not correctly, be termed depolymerization".

Twiss and Thomas investigated the relative activity of the various allotropic forms of sulfur, capable of existing within the range of temperatures used in vulcanization, toward rubber, and found that, although the three forms differed widely, the outstanding fact was the relatively small magnitude of their difference in activity.

In 1925, Twiss put forward his theory on vulcanization. He suggested that the physical effect of vulcanization is in part the outward manifestation of a chemical change in the rubber hydrocarbon, and that this change is induced by the chemical action of sulfur on a relatively small proportion of rubber. The induced reaction he considered to be a polymerization of the remaining caoutchouc molecules. The "rubber sulfide" produced is insoluble and is dispersed in what may approach a molecular condition throughout the rubber by vulcanization. The action of the rubber sulfide was regarded as similar to that played by carbon black in reinforcement, but because the sulfide is formed in situ, it is more effective in smaller quantities. Twiss's theory of vulcanization was one of various theories which appeared around this period, and, in common with others, had much to commend it, but like them it explained only part of the known facts. It subsequently formed a stepping-stone towards improved theories of a more comprehensive type, and in this respect may be regarded as one of the classical theories.

Subsequently, Twiss made many attempts to produce vulcanization by the formation of colloidal particles in rubber. He considered that vulcanization and reinforcement are interrelated, and that, for ideal reinforcement by a material formed within the rubber matrix, a number of conditions must be fulfilled; the substance must be insoluble in rubber and be colloiddally dispersed; its formation must be rapid, and the character of its surface satisfactory; the reactants must be soluble in the rubber so that the reaction can occur in the

rubber phase, and the dispersed substance must be chemically stable. He found that nickel carbonyl and lead tetraethyl, particularly in the presence of free sulfur, showed some promise, but the products did not fulfil all the necessary conditions for ideal reinforcement.

Twiss was fascinated with the possibility of forming active compounding ingredients *in situ* in rubber, and later he carried out many experiments to produce both vulcanizing and reinforcing ingredients, with rubber itself as the reaction medium. An example of this was the vulcanization of rubber at ordinary or slightly elevated temperatures by first compounding with sulfur, zinc oxide, and a secondary amine, or an easily decomposed compound of the amine, and then converting the latter into an ultra-accelerator by the action of carbon disulfide. He found that the carbon disulfide treatment not only led to the formation of the dithiocarbamate ultra-accelerator, but also further increased its activity for the rubber/sulfur combination. This result was found to be a general one for all thio accelerators and to be analogous to the activating effect of zinc oxide towards them.

From about 1929 onwards he investigated a number of methods for the control of accelerated vulcanization. Earlier he had shown that the incorporation of a caustic alkali, preferably dissolved in glycerol, in a rubber/sulfur mixing resulted in an increased rate of reaction on heating. He then investigated the reverse effect by the addition of organic acids and acidic salts to accelerated rubber/sulfur mixes in order to restrain "scorching" or prevulcanization. Another approach to the same problem was the investigation of a number of delayed-action accelerators.

With the commencement of what might be termed the latex era in the early 1920's, Twiss was quick to realize the possibilities of rubber in this new form. In 1925 he and his collaborators became interested in applications of centrifuged latex from Malaya, and, during the next three years, methods were evolved for producing compounded concentrated latexes that were employed in the manufacture of proofed fabrics and dipped goods. Some of this earlier work was described in a paper given by him at the Paris Conference on Rubber Technology in 1931.

Many of the investigations in the latex field by Twiss and his fellow workers are described in several patent specifications which during the period 1926 to 1930 followed each other in rapid succession. They contributed largely to the establishment of a thriving latex product industry in the United Kingdom, which include such important products as foam rubber and latex thread.

Twiss's work on latex was not, of course, confined to the development of practical applications. By investigating the electrophoretic behavior of diluted ammonia-preserved plantation latex, he and his collaborators were able to show that the amounts of protein and rubber resin adsorbed on the surface of the rubber globules depends on the degree of dilution of the latex and on the pH of the serum. Removal of ammonia, or subjecting the latex to dialysis, narrows the range of pH in which coagulation of preserved latex occurs with acetic acid. This range is broadened by addition of salts such as potassium sulfate or ammonium acetate, and these results are in accord with the view that the rubber particles carry an adsorbed protein layer. The delayed coagulant effect of sodium fluosilicate arises, not merely from the gradual development of acidity, but also from the concurrent formation of zinc ions. If the zinc ions became effective at too high a pH value, the coagula may be undesirably weak. This can be prevented by the additional presence of a sparingly

soluble zinc salt, *e.g.*, zinc sulfate. The coagulant activity of sodium fluosilicate can also be controlled by the addition of salts which decrease its solubility or its rate of hydrolysis.

Work carried out in 1935 to 1938 on creaming of preserved rubber latex showed that partial adsorption of the creaming agents occurs at the surface of the rubber globules. The creaming agent adsorbed in this way links with others of its own molecules in the serum to form a weak reticular structure, which eventually yields to buoyancy pressure.

In a review of the consequences of the electrical double layer in rubber technology, consideration was given to the effect of occurrence of electric charges on small particles, on the electrical coagulation and concentration of latex, the effect of dialysis on the pH at which coagulation takes place, and the part played by protein in the formation of a protective layer on the dispersed rubber particles.

In a paper published in 1945 entitled "The Role of Oxygen in the Plasticization of Rubber", he pointed out that there is some evidence that the rubber molecules or segments of the rubber molecules become more chemically active when they are subjected to strain by milling. This could be observed by the action of chemical agents such as sulfuric acid or sulfonic acid on rubber or even on replasticized vulcanized rubber. The reaction proceeds much more rapidly when the rubber is continuously stressed than when it is heated at the same temperature under static conditions.

Despite his high scientific attainments, Dr. Twiss was a modest and reserved man, and to those who knew him well he had many endearing qualities. He had an essentially kindly character, and would carry out unobtrusively many acts of kindness for those who needed help. He took an active part in the social activities of the church he attended, and in his earlier life was a lay reader.

Dr. Twiss had a quick and imaginative mind, with an undoubted sense of humor, and this made him an excellent conversationalist and lecturer. In his early days he played rugby football and cricket—a game that always held his interest, but above all his hobby, particularly in his later days, was reading.

The rubber industry lost one of its distinguished savants in the passing of Dr. Twiss.

ABRASION RESISTANCE OF GR-S VULCANIZATES *

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AND L. H. HOWLAND

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The practical aspects of compounding elastomers for use in fabricating rubberlike products involves a search for the combination of compounding ingredients and mixing and curing procedures that will produce the best vulcanizates. Quite often progress is retarded by the lack of satisfactory laboratory methods for evaluating vulcanizates and, in these cases, investigators have to rely on service performance tests as the only means for determining the relative merits of various compounding and curing modifications. Such a situation is exemplified by past and some present attempts to improve the wearing qualities of automobile tire treads containing various synthetic rubbers.

Prior to the time when synthetic rubbers were used extensively in tire-tread formulations, more than twenty different laboratory machines were developed and used for determining the abrasion resistance properties of natural rubber vulcanizates. Some utility was claimed for each machine, but the situation appeared hopeless when attempts were made to compare the abrasion resistance properties of vulcanizates containing other elastomers. It was generally found that the GR-S type of synthetics contaminated abrasive surfaces and caused unreasonable differences in abrasion resistance when rated against natural rubber. The work of Griffith and coworkers¹, later confirmed by Buist², indicated that the effects of the interfering track lubricants could be reduced by extracting the vulcanized test-specimens with ethyl alcohol-toluene azeotrope before abrading them under controlled conditions. The method appeared to be basically sound if it was assumed that tire treads in service were mechanically worn away by being continually exposed to fresh, unlubricated abrading surfaces. All workers do not subscribe to this theory because of water leaching, oxidation and (or) postvulcanization effects that are claimed to enter into over-all abrading processes. Since conclusive proof to support many of the suggested theories was lacking, an extensive program for evaluating various road-tested vulcanizates on laboratory abraders was undertaken to find a method for determining the abrasion resistance properties of reinforced GR-S vulcanizates, without resorting to the solvent extraction of test-specimens.

The prime requisite of any laboratory test is that the results correlate with actual service testing. Initial work on selecting vulcanizates for laboratory tests revealed that this requirement was difficult to fulfill because of testing discrepancies that appeared in abrasion resistance ratings obtained by actual road testing. Factors such as tire construction, vehicle characteristics, road conditions, locality and other variables discussed by Mandel, Steel, and Stiehler³, influenced tread wear to such an extent that a large number of tests were necessary to determine the average wear rating of any one type of vulcanizate. For this reason it was felt that there was little hope of reproducing

* An original contribution. This paper was presented before the Twelfth International Congress of Pure and Applied Chemistry, New York, N. Y., September 10-13, 1951.

service testing in the laboratory. On the other hand, there was a real need for a laboratory method that could be used for making a better selection of compounds for road testing, and it was toward this latter objective that the entire program was directed.

EVALUATION OF ABRASION MACHINES

When recently published papers on the abrasion resistance properties of vulcanizates were reviewed, it was observed that investigators generally agreed upon the shortcomings of laboratory abrasion test methods when applied to testing GR-S. It was also noted that one machine, specifically the Dunlop or Lambourn abrader⁴, had not been considered in many of the projects, for which reason this abrader was selected as one of the four abraders to be evaluated. The other three machines tested in preliminary work were the National Bureau of Standards⁵, du Pont⁶, and United States Rubber Company⁷ abraders.

A series of nine laboratory-mixed compounds containing four different types of GR-S and three different carbon blacks were prepared and vulcanized to obtain specimens for a testing program that was carried out in cooperation with the Columbian Carbon Company Laboratories, Brooklyn, N. Y., where an original Lambourn abrader was available. The evaluations of the National Bureau of Standards, du Pont, and United States Rubber abraders confirmed work already reported in that anomalous results were invariably obtained. Thorough analyses of recent unpublished data reported by other investigators who used various forms of the Goodyear angle abrader⁸ indicated that this type of machine was also unsatisfactory for comparing abrasion resistance properties of various elastomer vulcanizates. Some degree of correlation with reported road tests was indicated by the abrasion resistance determinations made using the Lambourn abrader. As a result of this work, a machine similar to the Lambourn was constructed from parts and accessories that could be obtained or fabricated in the United States.

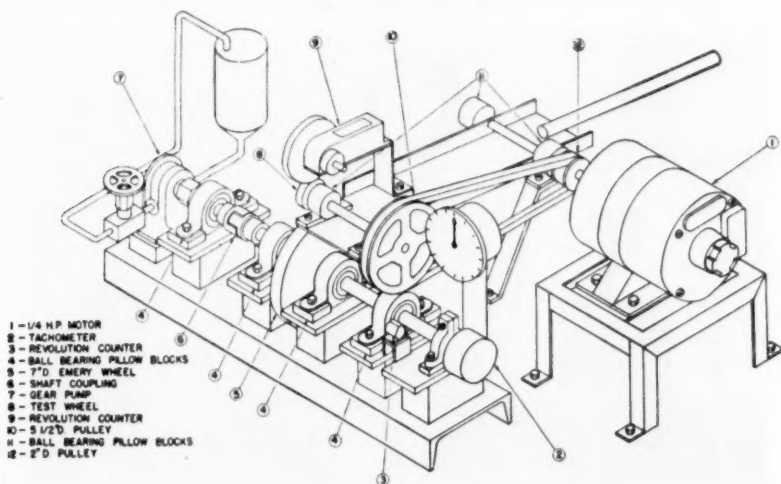
THE MODIFIED LAMBOURN ABRADER

The Dunlop or Lambourn abrader is essentially a device for driving a small molded and vulcanized test wheel on an abrasive wheel to which a continuous braking force is applied. Both wheels rotate in a vertical plane, with the test wheel running on the upper surface of the abrasive wheel. Revolution counters are required to determine test run and track travel distances. A tachometer is driven by the abrasive wheel shaft for the purpose of enabling the operator to control the slip between test wheel and track. Initial designs to build a modified machine differed from the original only in the following respects:

1. Provisions were made to drive the tachometer directly with the abrasive wheel shaft rather than by means of a belt.
2. Specifications called for installing a revolution counter equipped with a friction drive wheel, one foot in circumference, to ride on the test wheel for the purpose of conveniently determining test run distances.

The greatest difficulty in constructing a machine that would operate satisfactorily was encountered in finding a suitable braking device. Several electrical eddy-current brakes similar to the one used in the original Lambourn abrader were constructed and attached to the abrasive wheel shaft. Each one proved to be unsatisfactory, primarily because of the heat developed in the d.c. electromagnet coils. Among the other types of brakes that were evaluated,

the one that proved to be most satisfactory and had the simplest operating characteristics was a small gear pump through which oil was pumped in a circulatory system. With this unit the breaking forces were controlled by opening or closing a valve in the oil line on the discharge side of the pump. Specifications for the components used in constructing the abrader shown in the drawing, Figure 1, and photograph, Figure 2, were as follows (test wheel assembly shown slightly raised in the drawing):



MODIFIED LAMBOURN ABRADER

FIG. 1.

1. Split phase, $\frac{1}{4}$ h.p. electric motor operating at a constant speed of 1725 r.p.m. on 115 volt, single phase, 60-cycle a.c. General Electric Company Model 5KH-47AB256.
2. Tachometer assembly. Catalog No. 225, Model J stationary tachometer, 4-inch dial, range 20-200 r.p.m., furnished with Catalog No. 1462 4:1 increase shaft end take-off section and solid section No. 1630. Herman H. Sticht Co. Inc., 27 Park Place, New York 7, N. Y.
3. Revolution counter. Series No. 1007, small star-wheel type. Veeder-Root, Inc., Hartford 2, Conn.
4. Shaft bearings. Self-aligning precision ball-bearing type, Catalog No. BNS. Boston Gear Works Catalog.
5. Abrasion Wheel. Seven inch diameter, $\frac{3}{4}$ inch wide, aluminum oxide grinding wheel No. A 46-06-V30. The Carborundum Co.
6. Shaft coupling. Boston Gear Works Catalog No. FCR-12.
7. Braking assembly. Series 50, bronze gear pump No. 4. Oberdorfer Foundaries, Inc., Syracuse, N. Y. Stainless steel, 104 cu. in. tank, 5 in. diameter and 8 in. long. Ireland and Vice, Auburn, N. Y. An S.A.E. 60 viscosity motor oil was used in the pumping system.
8. Test wheel. Molded in molds made by Hoggson and Pettis, New Haven, Conn.

9. Revolution counter. Series 1110, worm driven counter with No. 1 rotation. Wing-nut reset, equipped with rubber-faced friction wheel one foot in circumference. Veeder-Root, Inc., Hartford 2, Conn.
10. Vee groove pulley. No. 550A, $5\frac{1}{2}$ in. diameter, $\frac{1}{2}$ in. bore. Patron Transmission Co., New York 13, N. Y.
11. Boston Gear Works ball bearing pillow blocks No. SRB8.
12. Vee groove pulley No. 200A, 2 in. diameter, $\frac{3}{8}$ in. bore. Patron Transmission Co., New York 13, N. Y.

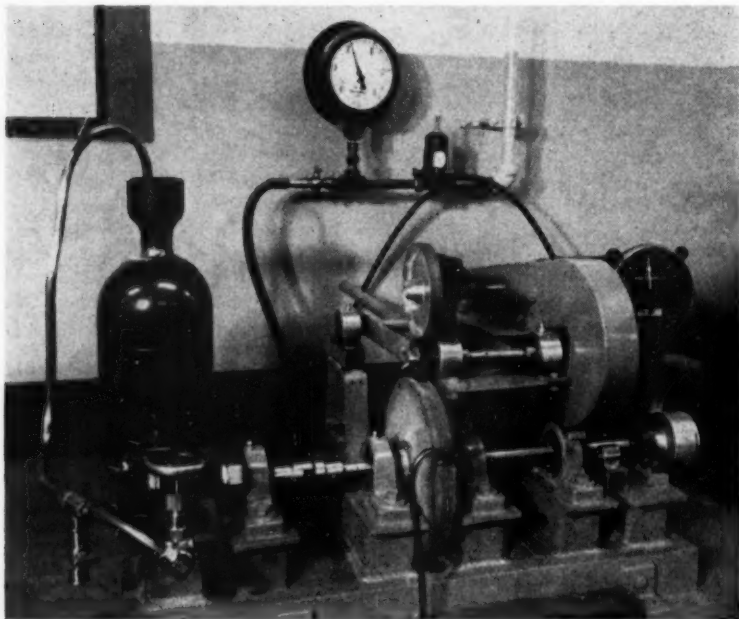


FIG. 2.

The entire machine was rigidly mounted on an iron clad, $\frac{3}{4}$ -inch plywood base and the abrasive wheel assembly was elevated on a piece of 2×6 inch channel iron. The 12-inch rod, $\frac{3}{8}$ inch in diameter, shown protruding from the rear of the pivoting test-wheel carriage, was attached to accommodate an adjustable weight that could be moved backward to reduce the load on the test wheel. Tests conducted after the machine was completed indicated that satisfactory abrading rates at the desired percentage slip were obtained without reducing the load on the wheel. For this reason the weight was omitted in the drawing.

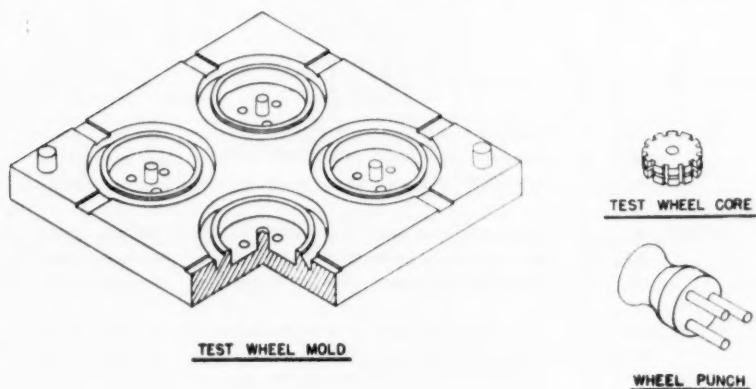
PREPARATION OF TEST SPECIMENS

Test wheels $1\frac{1}{4}$ inches in diameter and $\frac{3}{8}$ inch thick were prepared in molds very much like those described by Lambourn. Four-cavity molds, aluminum wheel cores, and a knock-out punch as shown in Figure 3 were constructed by Hoggson and Pettis Manufacturing Company, New Haven, Conn. Compounded elastomer stocks for molding into wheels were sheeted out on a 12-

inch laboratory rubber mill with the rolls set 0.055 inch apart. Strips of the stock, approximately 12 inches long and 0.5 inch wide, were cut and each was wrapped around a wheel core until a wheel that could be forced into the mold cavity was obtained. The "tires" were then press-cured for the desired length of time at a temperature of 292° F in molds that had been coated with a dilute emulsion of Dow-Corning Mold Release 35A. After curing, the mold covers were removed and the wheels were knocked out with a punch and quenched in cold water. Excess overflow flanges of stock were cut from the tires with scissors before subjecting the wheels to a conditioning run of 1000 feet at 24 per cent slip on the abrader.

TEST PROCEDURE

Investigations carried out at the Columbian Carbon Company laboratories indicated that the best condition for testing vulcanizates on this particular



ACCESSORIES FOR MODIFIED LAMBOURN ABRADER

FIG. 3.

machine were at skid or slip values between 20 and 25 per cent. It was found that running test wheels for 3000 feet at 24 per cent slip with a 3500-gram load, required 10 minutes of abrading to wear off from 0.04–0.60 gram of vulcanizate, depending on the wearing property of the material. These conditions for determining abrasion resistance properties were considered to be the most convenient and least vulnerable to experimental errors."

Actual testing was carried out as outlined in the sample work sheet, Figure 4, where the initial weight of the conditioned test wheel and the initial reading of the track revolution counter (R_1) were entered before the wheel was abraded. The counter for recording test travel distances was reset to zero, after which the test wheel was fixed securely to the drive shaft and lowered to contact the abrasive track. A sustained braking force was applied to the abrasive wheel during the run to reduce its speed to 100 r.p.m. This was accomplished by manually controlling the flow of oil through the gear pump line by means of a valve. Talc was applied to all test wheels with a small camels' hair brush at

intervals of 500 feet to remove abraded material that, at times, was found to adhere to the tread surface. Air under 6 lb. per sq. in. pressure, directed on to the face of the abrasive wheel by means of two jets constructed from copper tubing, proved to be satisfactory for cleaning the track. After a test run of 3000 feet was finished, the machine was stopped and the final track revolution counter reading (R_2) was entered on the test sheet. The wheel was then removed and cleaned with a brush before weighing.

Specific gravity determinations required for converting weight loss values (grams) to volume loss (cubic centimeters) were made by a "sink-float" method, in which small bits of vulcanizate cut from the abraded wheel were wet in a 0.5 per cent solution of Tergitol No. 7 (Carbide and Carbon Chemicals Corp., New York, N. Y.) and filtered out on cheesecloth. The pieces were blotted on absorbent paper and dropped into zinc chloride solutions covering the

ABRASION RESISTANCE TEST WORK SHEET												
SAMPLE	WHEEL NUMBER	R ₁	R ₂	R ₁ -R ₂	TRACK TRAVEL (1) (R ₂ -R ₁) 183	WHEEL WT. BEFORE TEST	WHEEL WT. AFTER TEST	WT. LOSS, GMS. (w)	SPECIFIC GRAVITY (s)	VOL. LOSS, cc w/s	TEST RUN DISTANCE, (d)	% SLIP $\frac{(d-1)100}{d}$
XT 408	30	1	13035	1272	1237	2260	239145	237820	1365	1113	1760	24.6 %
	60	4	24965	26191	1246	2260	240170	238825	1345	1115	1475	24.0 %
	90	11	30741	51996	1255	2300	238005	236640	1365	1115	1675	23.3 %
XT 409	30	5	14272	15530	1258	2300	243220	234800	7800	1130	6380	23.5 %
	60	13	26191	27436	1245	2280	239140	236990	1750	1130	2413	24.0 %
	90	8	36353	37594	1241	2270	241315	239960	1355	1130	1740	24.3 %
XT 410	30	8	15530	16776	1246	2280	239835	237335	2600	1125	2310	24.0 %
	60	17	27436	28685	1249	2290	242755	241990	1565	1125	1210	23.6 %
	90	18	37594	38851	1257	2300	240810	239500	1060	1125	943	23.5 %
XT 415	30	16	16776	18014	1238	2260	240393	238565	1828	1135	6000	24.6 %
	60	14	28685	29929	1244	2280	240280	237925	1585	1135	2100	24.0 %
	90	5	38851	40111	1260	2305	242050	240350	1680	1135	1480	23.2 %

FIG. 4.

specific gravity range of 1.05 to 1.20 at intervals of 0.01 gram per cubic centimeter. The specific gravity of the solution in which the vulcanizate had a tendency neither to float nor sink was used as the specific gravity of that particular stock. After specific gravity values were obtained the cores were removed from the test wheels for future use.

CALCULATION OF RESULTS

It was found necessary to control the amount of slip between test wheels and the abrasive track as closely as possible at 24 ± 1 per cent. For this reason the slip values reported in the last column of all testing sheets were calculated first to check the performance of the abrader before attempts were made to analyze abrasion loss data.

Preliminary tests revealed that abrading rates of GR-S vulcanizates were influenced to a large extent by the state of cure of the compounds. It was

because of this factor that each set of abrasion loss values had to be considered in light of the curing characteristics of the particular stock being evaluated. When the times of cure or states of cure at which ratings were to be made were selected, volume abrasion loss values were compared to similar values for a standard stock. Since laboratory wear ratings obtained by comparing volume losses magnified differences between vulcanizates, adjustments were made in the calculations to bring the results more in line with reported tire-tread wear ratings. One-half of the difference between the volume abrasion losses of the standard vulcanizate and the vulcanizate to be rated was added to the smaller value to obtain an adjusted loss figure. The quotient of the actual volume loss of the standard divided by the adjusted figure was multiplied by 100 to obtain an abrasion index or rating. A simplified equation for calculating ratings is shown below:

$$\text{Rating} = \frac{200 V_s}{V_a + V_s}$$

where: V_s = volume abrasion loss of standard.

V_a = volume abrasion loss of vulcanizate rated.

Ratings higher than 100 indicated superiority over the standard, whereas, ratings less than 100 indicated inferiority.

PRECISION OF TESTING

One experiment planned to determine the precision of testing with the modified Lambourn abrader included testing vulcanizates from compounds of five different types of GR-S. The elastomers used in this work were prepared by copolymerizing emulsified butadiene and styrene at a temperature of 5° C to 60 per cent conversion. Formula modifications were made to produce copolymers with raw Mooney viscosities of 40, 60, 80, 100, and 120. The following formula was used for compounding all stocks that were subsequently molded into test wheels and cured for the times specified in Table I.

GR-S	100
Easy-processing channel black	50
Zinc oxide	5
Sulfur	2
Stearic acid	1.5
Benzothiazolyl disulfide	3.0

The three wheels that were prepared for each time of cure were not cured in the same heat; i.e., the second wheel of compound UY-40 cured for 40 minutes, was not cured at the same time that the first wheel was. Testing was also done in a random fashion in that no attempt was made to abrade a standard stock in each series nor was any one group of wheels abraded on the same day. Individual ratings as shown in Table I and summarized in Table II indicated that a spread of 6.45 percentage units or a deviation of ± 3.2 units could be expected when random samples were abraded. More precise testing was indicated when the three very great differences appearing in the 60-minute cure column were excluded from the analysis of data.

Information regarding the effect of Mooney viscosity on the abrasion resistance properties of vulcanizates was also obtained in this experiment. The data shown in Table II indicated that an improvement of 12 per cent in abrasion resistance was realized by preparing vulcanizates from GR-S having a Mooney viscosity of 120 rather than 40.

TABLE I
PRECISION OF TESTING WHEELS AT RANDOM

Compound	Abrasion resistance ratings, % of Standard*			
	40-min. cure ^b	60-min. cure	80-min. cure	110-min. cure
UY-40	92	110	102	103
	97	107	99	96
	91	107	101	96
Average rating	93	108	101	98
Δ^c	6	3	3	7
UB-60	110	107	103	109
	104	110	99	107
	103	97	103	110
Average rating	106	105	102	109
Δ	7	13	4	3
UZ-80	109	99	111	107
	107	101	105	109
	108	107	110	102
Average rating	108	102	109	106
Δ	2	8	6	7
UU-100	108	125	108	113
	109	111	106	118
	104	108	109	111
Average rating	107	115	108	114
Δ	5	17	3	7
UX-120	108	125	108	116
	100	117	111	114
	112	114	104	110
Average rating	107	119	108	113
Δ	4	11	7	6

* Average of abrasion loss values of UY-40, used as a standard.

^b Curing temperature, 292° F.

^c Spread between triplicate determinations.

A second series of tests were conducted to determine the average difference between duplicate ratings when efforts were made to reduce curing and abrading errors. Two test wheels were prepared from each of ten different laboratory mixed GR-S compounds by curing duplicate wheels for 60 minutes in the same mold. Abrasion resistance ratings obtained by curing in this manner and abrading the wheels in consecutive order indicated (Table III) that an average spread of 4.3 percentage units, or a deviation of ± 2.2 units, could be expected.

TABLE II
PRECISION OF TESTING WHEELS AT RANDOM
(Summary of data)

Compound	Grand average of ratings	Average Δ
UY-40	100	
UB-60	106	
UZ-80	106	
UU-100	111	
UX-120	112	

6.45 or ± 3.2

Subsequent testing carried out following this procedure confirmed the precision noted above.

EVALUATION OF TEST METHOD

Twenty factory-mixed tread compounds prepared by the Lakeshore Tire and Rubber Co., Des Moines, Iowa, for the government tire test projects described by Mandel, Steel, and Stiehler³ were obtained from the National Bureau of Standards. The stocks selected for the evaluation were GR-S 10, GR-S, natural rubber (Hevea) and GR-S X-485 (copolymer made at 5° C) compounded with three different high abrasion furnace (HAF) blacks, one rein-

TABLE III
PRECISION OF TESTING WHEELS CONSECUTIVELY

Compound	Abrasion resistance ratings, % of standard	Difference between duplicate ratings (Δ)
B-579	105	3
	102	
B-580	106	2
	104	
B-581	103	1
	102	
B-582	97	7
	90	
B-583	101	0
	101	
B-584	100	7
	93	
B-585	133	15
	118	
B-587	118	2
	116	
B-588	116	5
	111	
B-589	92	2
	94	
Average		4.3, or ± 2.2

forcing furnace (RF) black and one easy processing channel (EPC) black. Test wheels were prepared from all twenty compounds cured 30, 60, and 90 minutes at 292° F, and the abrasion loss for each wheel was determined. The wheels cured for 30 minutes generally exhibited poor resistance to abrasion properties, for which reason average volume loss values for the wheels cured 60 and 90 minutes were used for calculating ratings.

Road wear ratings reported by the Office of Rubber Reserve⁹ were calculated, using skid losses for GR-S 10 treads containing HAF black No. 1 as the rating standards (assigned value 100 per cent). All other treads were rated with respect to these stocks. A separate rating standard was used for each

TABLE IV
TIRE WEAR AND ABRASION RESISTANCE PROPERTIES OF VULCANIZATES

Tire code	Carbon black	Elastomer	Skid loss	Tire wear rating	Laboratory abrasion rating
VBC-1I1	HAF No. 1	GR-S 10	0.164*	100	—
VBD-1I2	HAF No. 1	GR-S 10	0.181		100*
VBD-1E1	HAF No. 1	GR-S	0.160	103	84
VBD-1A2	HAF No. 1	Hevea	0.155	106	98
VBD-1M1	HAF No. 1	X-485	0.137	120	116
VBC-1K1	HAF No. 2	GR-S 10	0.175	94	113
VBC-1G2	HAF No. 2	GR-S	0.160	103	91
VBC-1C2	HAF No. 2	Hevea	0.154	106	103
VBC-1O1	HAF No. 2	X-485	0.136	121	127
VBD-1J1	HAF No. 3	GR-S 10	0.168	98	96
VBD-1F1	HAF No. 3	GR-S	0.172	95	89
VBD-1B1	HAF No. 3	Hevea	0.152	108	94
VBD-1N1	HAF No. 3	X-485	0.128	128	120
VBC-1L1	RF	GR-S 10	0.167	98	105
VBC-1H1	RF	GR-S	0.160	103	105
VBC-1D1	RF	Hevea	0.192	85	84
VBC-1P1	RF	X-485	0.136	121	115
VBC-1J1	EPC	GR-S 10	0.192	85	87
VBC-1F1	EPC	GR-S	0.188	87	64**
VBC-1B1	EPC	Hevea	0.228	72	85
VBC-1N1	EPC	X-485	0.190	86	86

* Rating standards.

** This value excluded from subsequent analysis.

series of tires (VBC and VBD, Table IV), whereas only one standard (VBD) was available for laboratory testing. The skid loss value of 0.181 for the standard in series VBD appeared to be out of line with loss values for GR-S 10 stocks containing HAF carbon blacks. For this reason, and the fact that all of the tires travelled approximately the same distances, the skid loss value of 0.164, for the VBC series standard, was used for computing all tire wear ratings.

Ratings for individual stocks as shown in Table IV were grouped and averaged to obtain the ratings for each carbon black and elastomer shown in Table

TABLE V
CARBON BLACK AND ELASTOMER WEAR RATINGS

Carbon black	Wear rating	
	Tires	Laboratory
HAF No. 1	107	100
HAF No. 2	106	109
HAF No. 3	107	100
RF	102	102
EPC	83	86
Elastomer		
GR-S 10	95	100
GR-S	98	92
Hevea	95	93
X-485	115	113

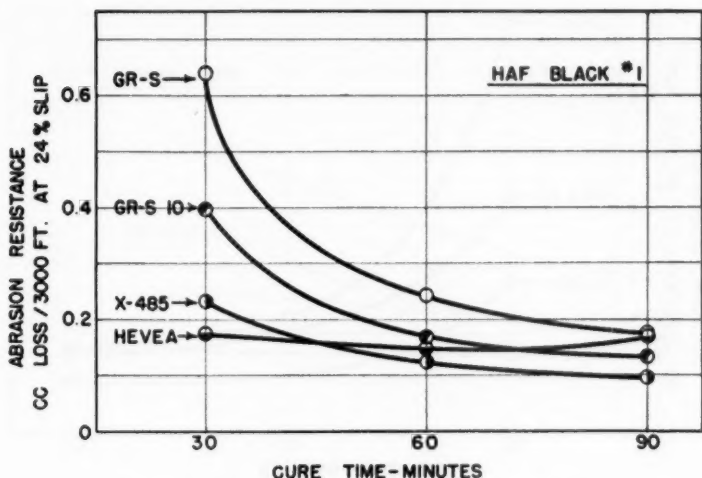


Fig. 5.—Abrasion resistance of reinforced elastomer vulcanizates.

V. The greatest difference between the service and laboratory test values reported in Table V was 7 per cent. The other five cases, where agreement was considered to be excellent, constituted the first evidence of a somewhat satisfactory test method.

Figures 5 through 9 illustrate the changes in abrasion resistance with times of cures for vulcanizates from compounds of each carbon black in the four different elastomers. It was evident that vulcanizates containing standard GR-S exhibited the greatest increase in abrasion resistance with longer times of cure and those containing Hevea showed very little change. The group of

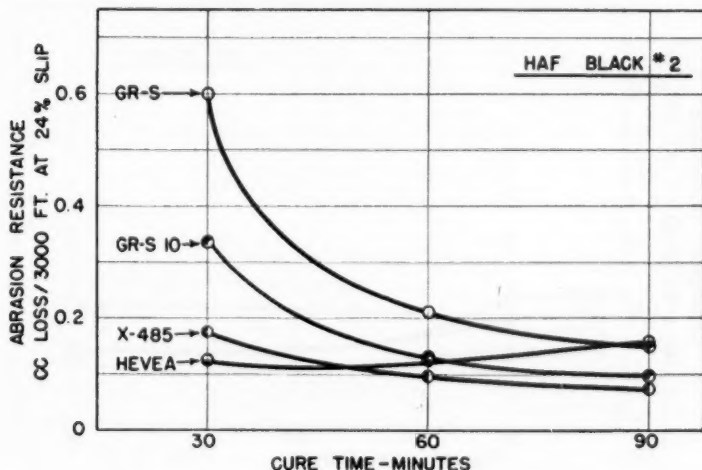


Fig. 6.—Abrasion resistance of reinforced elastomer vulcanizates.

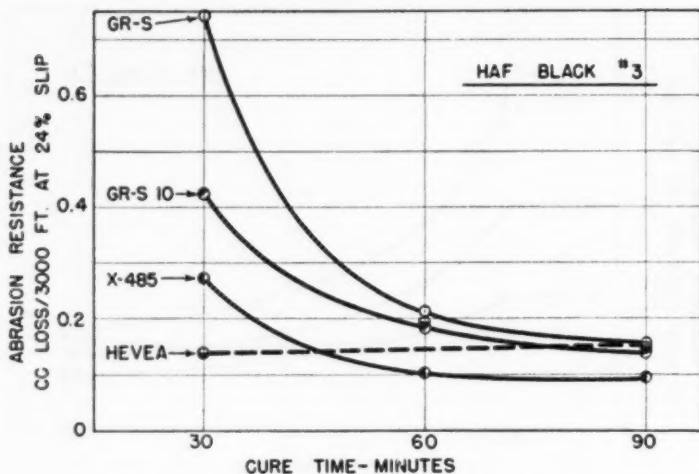


Fig. 7.—Abrasion resistance of reinforced elastomer vulcanizates.

curves of each of the three HAF carbon blacks were similar with respect to shape, but the groups were placed at different locations on the graphs, due to slight differences in quality of the carbon blacks. All compounds containing RF carbon black were prepared by a high-temperature mixing process that appeared to level out the abrasion resistance—time of cure curves for vulcanizates from these stocks. The graphs served to illustrate the effect of cure on abrasion resistance and emphasize the importance of selecting the proper point at which to compare vulcanizates.

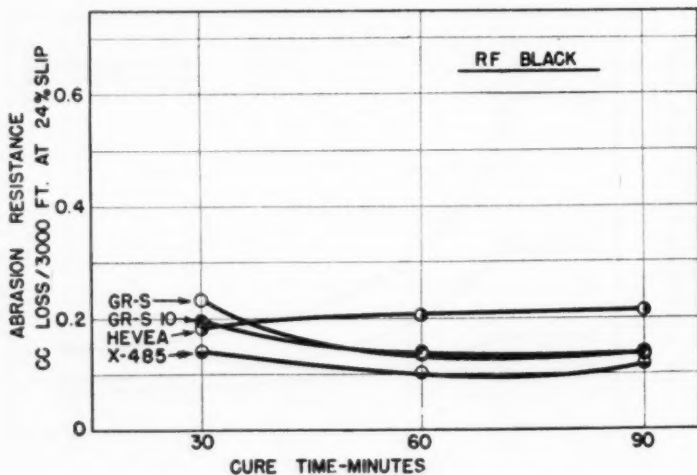


Fig. 8.—Abrasion resistance of reinforced elastomer vulcanizates.

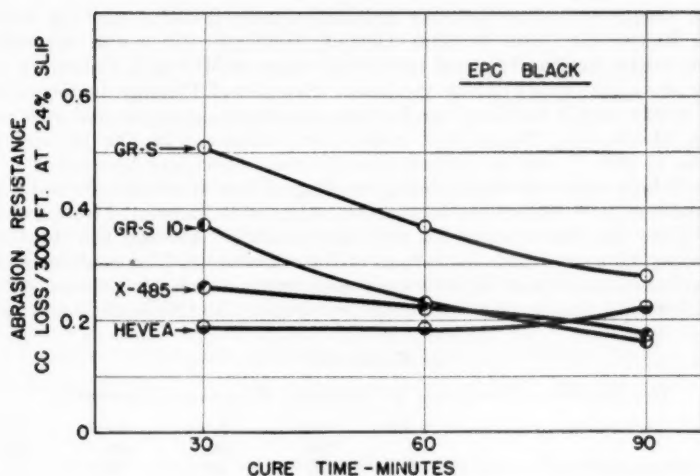


FIG. 9.—Abrasion resistance of reinforced elastomer vulcanizates.

The road tests reported in Table IV were made by the Government Tire Test Fleet in the vicinity of San Antonio, Texas, and represented testing only in that locality. In view of the fact that climatic conditions influenced the rate

TABLE VI
TIRE WEAR AND ABRASION RESISTANCE PROPERTIES OF VULCANIZATES

Stock features		Tire wear rating	Laboratory abrasion resistance rating
Project 65			
Natural rubber stock	No. 1	100	100
	No. 2	91	82
	No. 3	92	82
L. T. GR-S stock	No. 1	118	116
	No. 2	119	112
	No. 3	114	106
Project 91			
Natural rubber control		100	100
Natural rubber—L. T. GR-S			
Blend	No. 1	101	100
	No. 2	101	104
L. T. GR-S stock	No. 1	119	112
	No. 2	118	121
Project 103			
L. T. GR-S	No. 1	100	100
	No. 2	100	98
	No. 3	111	107

of tire wear, a second project was undertaken in cooperation with the United States Rubber Co., Tire Division, Detroit, Michigan, which was designed to include testing aged and unaged tires in the states of Michigan, California, and Texas at various times during the year. Samples of fourteen factory-mixed tread stocks used in building tires for this project were obtained and evaluated in the laboratory. Molded test wheels were cured for 25, 50, 75, and 100 minutes at 292° F, and the abrasion loss for each wheel was determined.

Prior information revealed that postcuring of tires in service affected wearing qualities, for which reason laboratory ratings were calculated from average loss values for wheels cured 75 and 100 minutes. Average tire wear and laboratory abrasion-resistance ratings of the vulcanizates that contained various carbon blacks (Table VI) indicated much better correlation between service and laboratory testing than was shown previously. In this work, it was again

TABLE VII
THE EFFECT OF SOFTENERS ON ABRASION RESISTANCE PROPERTIES

Compound		B-509	B-515	B-516	B-517	B-518
X-537		100	100	100	100	100
HAF carbon black		50	50	50	50	50
BLE		1.5	1.5	1.5	1.5	1.5
Marasperse-CB		1.5	1.5	1.5	1.5	1.5
Softener A		—	5	10	—	—
Softener B		—	—	—	5	10
Compounded Mooney viscosity		78	65	60	72	59
300% modulus	25' cure	730	640	600	830	390
(lb. per sq. in.)	50'	1390	1310	1210	1510	930
(cured at 292° F)	100'	2260	2110	1940	2310	1570
Tensile strength	50'	3490	3410	3280	3320	3170
(lb. per sq. in.)	100'	3630	3220	3430	3370	3340
Elongation (%)	50'	600	600	610	540	750
	100'	440	400	480	410	560
Abrasion loss	60'	0.074	0.097	0.131	0.080	0.112
(cc./3000 ft.)						
at 24% slip						
Abrasion rating		100	87	72	96	80

observed that vulcanizates containing natural rubber exhibited the least change in abrasion resistance with increasing cure times.

RESEARCH APPLICATIONS

One application of the modified Lambourn abrader to the investigation of polymerization variables, namely, the effect of GR-S viscosity on abrasion resistance properties, was discussed under precision of testing. Aside from this application, two others will be cited as typical examples of similar investigations. In the first case, the effects of two rubber softeners on the abrasion properties of GR-S vulcanizates were studied. Five latex incorporated carbon black masterbatches were prepared by flocculating mixtures of GR-S latex copolymerized at 5° C, HAF carbon black slurries and, when required, softener emulsions. The masterbatches were prepared as described previously¹⁰ ac-

cording to the formulation shown in Table VII and were compounded as follows:

Masterbatch	150
Zinc oxide	3
Sulfur	2.5
Benzothiazolyl disulfide	1.5
Stearic acid	2.0

Test wheels from each compound were cured for 60 minutes at 292° F, at which point all vulcanizates had good tensile strength properties. The abrasion ratings indicated that vulcanizates containing rubber softener A were inferior to those containing softener B.

Two latex incorporated carbon black masterbatches were subjected to extensive compounding experiments for the purpose of selecting formulas for preparing vulcanized test-specimens. Both products, X-537 and X-571 GR-S, were composed of 100 parts of GR-S (manufactured at 5° C) and 55 parts of an HAF carbon black. The two differed in that the latex used for X-537 was

TABLE VIII
EFFECT OF ACCELERATOR LOADING ON ABRASION RESISTANCE

Compound	X-537			X-571		
	A	B	C	A	B	C
X-537 masterbatch	155	155	155	—	—	—
X-571 masterbatch	—	—	—	155	155	155
Zinc oxide	3	5	5	3	5	5
Sulfur	2.5	2.0	2.0	2.5	2.0	2.0
Benzothiazolyl disulfide	1.5	—	—	1.5	—	—
Tetramethylthiuram disulfide	—	0.15	0.2	—	0.15	0.2
Stearic acid	2.0	—	—	2.0	—	—
Compounded Mooney viscosity	86	91	96	86	89	89
300% modulus						
25' cure	1020	280	730	1090	310	510
(lb. per sq. in.)						
50'	1990	760	1340	1770	680	1180
(cured at 292° F)	100'	1180	1690	2530	970	1530
Tensile strength						
25'	2540	520	1610	2590	510	1050
(lb. per sq. in.)						
50'	3530	1760	2750	3330	1340	2620
100'	3790	2400	3090	3610	1960	2730
Elongation (%)						
25'	610	700	600	600	610	620
50'	500	600	550	510	580	600
100'	380	560	500	400	560	500
Abrasion loss						
(cc./3000 ft.						
at 24% slip)						
35'	0.069	0.168	0.093	0.069	0.169	0.088
45'	0.070	0.168	0.107	0.070	0.152	0.097
60'	0.071	0.088	0.069	0.058	0.121	0.079
80'	0.060	0.112	0.065	0.077	0.132	0.088
110'	0.065	0.114	0.071	0.061	0.126	0.085
130'	0.072	0.100	0.072	0.059	0.128	0.086
Abrasion rating	100*	78	98	102	69	88

* Standard.

shortstopped with dinitrochlorobenzene, whereas latex for X-571 was shortstopped with hydroquinone plus hydrogen peroxide.

The investigations were centered around testing vulcanizates from compounds containing various loadings of the vulcanization accelerators benzo-thiazolyl disulfide (MBTS) and tetramethylthiuram disulfide (TMTS). Several examples (Table VIII) were chosen from this project to illustrate the effect of acceleration on the physical properties of vulcanizates. Six molded test wheels from each compound were cured for various times between 35 and 130 minutes for abrasion testing. The actual abrasion loss values and ratings, calculated from averages of results for the 60, 80, 110, and 130-minute cures,

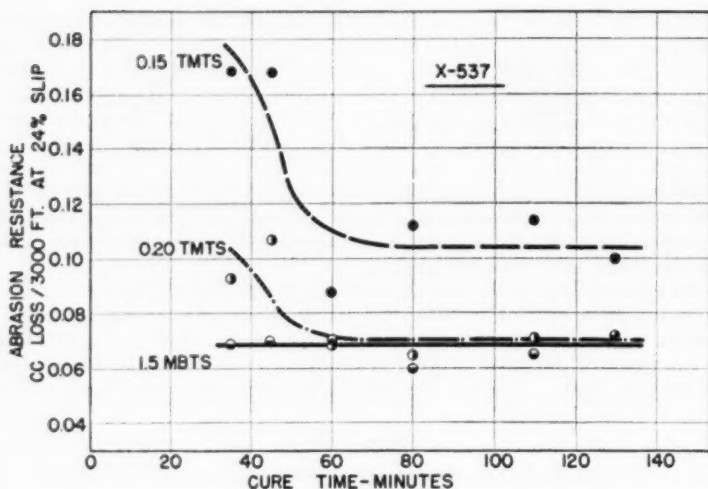


Fig. 10.—Effect of accelerator loading on abrasion resistance.

indicated that vulcanizates from the compounds containing the highest accelerator loading exhibited the best quality with respect to abrasion resistance.

The shapes and positions of the curves obtained by plotting abrasion losses versus times of cure (Figures 10 and 11) indicated that optimum abrasion resistance properties were reached at different levels. Vulcanized masterbatches compounded with 1.5 parts of benzothiazolyl disulfide, an amount of accelerator that was considered to be adequate, exhibited good and equivalent abrasion

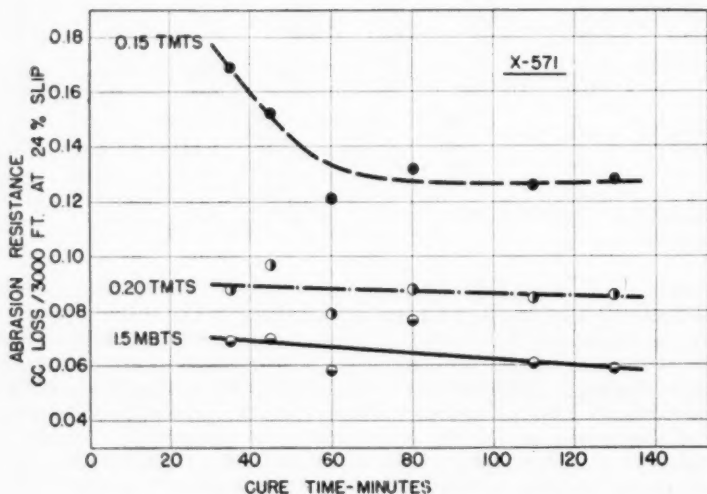


Fig. 11.—Effect of accelerator loading on abrasion resistance.

resistance properties; even at the early cures where 300 per cent modulus values were about 1000 lb. per sq. in., good abrasion resistance was shown. On the other hand, poor abrasion resistance properties were exhibited by vulcanizates from stocks compounded with an insufficient amount of accelerator, 0.15 part tetramethylthiuram disulfide. Test wheels cured for 110 minutes, where 300 per cent moduli were about equivalent to those for the 25-minute vulcanizates containing 1.5 parts benzothiazolyl disulfide, were definitely inferior.

This comparison of two different accelerators revealed that proper amounts of each were required in compounding to impart similar rates of cure as measured by modulus. It did not appear that a good comparison could be made by selecting cures of equal modulus for abrasion testing when the cure rates differed considerably. Vulcanizates exhibiting similar resistance to abrasion properties could be prepared with either type of accelerator employed in this project, as was done in compounding X-537. These examples serve to stress the importance of selecting good compounding formulas that include proper amounts of accelerators.

CONCLUSIONS

Data obtained from testing vulcanizates on the modified Lambourn abrader established that it was better than most laboratory devices for determining the effect of carbon blacks, elastomers, and other compounding variables on abrasion resistance properties as compared to tire wear resistance. More specifically, in the field of evaluating GR-S stocks, a partial solution of the often-termed "hopeless problem" of rating different vulcanizates with regard to wear was evidenced in the results.

SUMMARY

A method for determining the abrasion resistance properties of reinforced vulcanizates was required for evaluating new GR-S type elastomers and carbon blacks developed for use in automobile tire treads. In spite of the fact that past experiences revealed that most laboratory machines are unsatisfactory for testing GR-S vulcanizates, a program for evaluating several machines was undertaken. A Lambourn abrader similar to the one recently adopted by the British Standards Institution¹¹ for testing elastomer vulcanizates appeared to be most promising, for which reason efforts were expended on constructing a similar machine.

The abrader that was constructed and operated to simulate wear brought about by a tire slipping on road surfaces embodied the following four modifications of the British machine:

1. All parts and accessories were either obtained or fabricated in the United States.
2. The electrical eddy current type of brake used in the original Lambourn machine was replaced with a hydraulic, gear pump braking system.
3. Intermittent talcing of the test wheel during operation was specified.
4. A revolution counter equipped with a friction drive wheel, one foot in circumference, was installed to ride on the test wheel for the purpose of conveniently determining test run distances.

The conditions for testing vulcanizates were standardized to obtain abrasion loss values that could be expressed in terms of loss in cubic centimeters per 3000 feet of running at 24 per cent slip. Adjustments were made in calculating

abrasion ratings from volume loss values to bring them more in line with reported service test ratings.

ACKNOWLEDGMENT

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Many individuals in several organizations cooperated in the program. The Columbian Carbon Company, particularly C. W. Sweitzer, deserves credit for granting permission to use their Lambourn abrader and for assisting in the initial evaluations. Personnel of the mechanical, electrical, engineering, research and physical testing departments of the United States Rubber Company, Synthetic Rubber Plant, served important roles in constructing and evaluating the modified abrader. J. E. Helquist's suggestion of using a gear pump brake is considered to be an important contribution. Comparisons between laboratory and service abrasion ratings were made possible through the efforts of personnel at the National Bureau of Standards and United States Rubber Company, Tire Division, where projects were coordinated by R. D. Stiehler and J. W. Temple, respectively. The assistance of all participants, including those whom space does not permit mentioning, is deeply appreciated.

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STUDIES OF THE VULCANIZATION OF RUBBER *

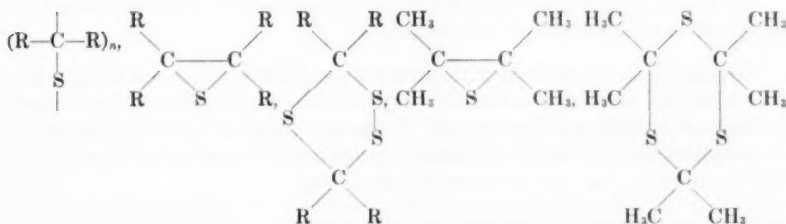
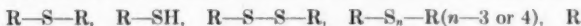
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In 1945, in our study of surface treatments of vulcanized rubber¹, we observed that vulcanized rubber, from soft to hard, is easily oxidized and decomposed into low-molecular fragments by hydrogen peroxide (35% H_2O_2) in glacial acetic acid or sulfuric acid. Later, we observed that the physical properties of soft vulcanizates improved with time when immersed in concentrated hydrazine hydrate solution². Since an explanation of these phenomena by previously postulated mechanisms of vulcanization seemed to be difficult, we have undertaken fundamental research on this subject. The difficulty encountered in carrying out this study has been the lack of a systematic method for the clear discrimination of the state in which the sulfur atoms are combined in various types of organic sulfur-containing compounds.

A study to analyze, by means of chemical reactions, the state of combined sulfur first performed on simple organic compounds consisting only of carbon, hydrogen, and sulfur. For comparative observations with vulcanized rubber, aliphatic compounds, especially those analogous to isoprene in structure, are preferable as model compounds. From this standpoint the investigations of Farmer and Bloomfield³ are to be highly regarded. However, the reaction products of olefins and sulfur are not only difficult to purify, but they are also almost impossible to isolate so that their structure can be identified. As will be discussed below, although we believe that a thioketone type of sulfur plays an important role in vulcanized rubber, it is very difficult to obtain a stable thioketone of the aliphatic series. For these reasons, in many examples, we have chosen model compounds of the aromatic type for the reactions with sulfur, but in our discussion of the reactions, all observations of the phenomena were made from the standpoint of the aliphatic series in mind.

The types of sulfur compounds used in the various reactions were as follow:



where R is  or 

* This paper is an original contribution, and comprises a review of important studies by Shu Kambara and his associates which have been published in the form of numerous individual papers and which can be

As the result of oxidation and other reactions carried out on these typical organic sulfur compounds, the following facts were observed.

(1) When oxidized with a mixture of hydrogen peroxide (35% H_2O_2) and glacial acetic acid, thiobenzophenone is converted into benzophenone, and the combined sulfur is eliminated quantitatively⁴ as $\text{SO}_4^{''}$. In the case of a polysulfide containing 3 or 4 atoms of the chain type of sulfur, the combined sulfur also is partly eliminated⁵ as $\text{SO}_4^{''}$. Other types of combined sulfur given above are not removed by this oxidizing agent. However, the distillate of the tri-thioacetone or trithiomethylethylketone distilled under normal pressure contains compounds containing combined sulfur, which is given off as $\text{SO}_4^{''}$ by oxidation⁶.

(2) Hydrazine (95% $\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$) reacts with thiobenzophenone at room temperature, giving hydrazone, with evolution of hydrogen sulfide⁷. Polysulfides, *e.g.*, $-\text{S}_3-$, $-\text{S}_4-$, lose part of their combined sulfur⁸, and thiols are converted into disulfides by hydrazine hydrate.

(3) Desulfurizing agents for thioketone, such as mercury and sodium sulfite⁸, act similarly toward polysulfides, but thioketone may be characterized by the fact that it is converted to ketone by these agents.

By the application of these reactions to natural rubber, which was vulcanized with sulfur alone under ordinary curing conditions which prevented the formation of hydrogen sulfide, and was then extracted with acetone to remove free sulfur and other foreign substances, the following facts⁹ were confirmed qualitatively or quantitatively:

(a) Sulfur is combined with rubber in at least two different states.

(b) If they are called the α -type and β -type, respectively, the α -type of combined sulfur under heat, or even when left to stand, changes gradually into the β -type.

(c) Vulcanized rubber, when treated with a mixture of hydrogen peroxide (35% H_2O_2) and glacial acetic acid, decomposes by oxidation, while the α -type of combined sulfur is quantitatively eliminated as $\text{SO}_4^{''}$.

(d) In ebonite containing about 32 per cent combined sulfur, the ratio of the α - to the β -type is approximately 1:2, but even in this case it is possible to convert the α -type gradually into the β -type by heating.

(e) When soft vulcanized rubber is immersed in hydrazine hydrate (95% $\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$), the α -type of combined sulfur reacts with hydrazine, forming a new nitrogen bridge within the rubber.

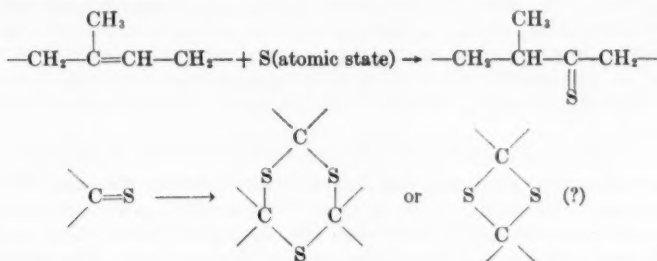
(f) The α -type of combined sulfur is easily removed as $(\text{CH}_3)_3\text{SI}$ by the action of methyl iodide.

(g) The α -type is also easily removed by heating with alcoholic potash or by oxidation with potassium permanganate¹⁰.

Comparing these reactions with that of low-molecular sulfur compounds, the α -type corresponds to thioketone and the β -type to the thioether bridge formed by the transformation of the former. From the analysis of infrared absorption of vulcanized rubber, Sears¹¹ had already predicted the existence of thioketone, but its existence may also be expected chemically.

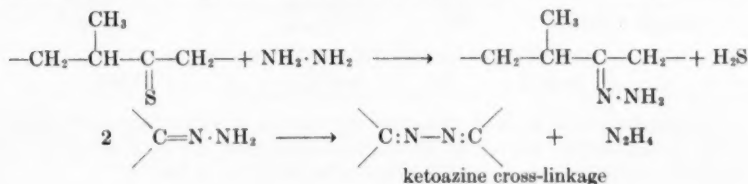
identified for the most part by the bibliography at the end of this paper and by reference to *Chemical Abstracts*. RUBBER CHEMISTRY AND TECHNOLOGY wishes to make known its appreciation of the aid and co-operation of the B. F. Goodrich Company, and of Dr. W. L. Semon of the B. F. Goodrich Research Center in particular, for first bringing to light this review and for being instrumental in obtaining it and offering it to RUBBER CHEMISTRY AND TECHNOLOGY. Likewise, thanks are due the author for his willingness to have RUBBER CHEMISTRY AND TECHNOLOGY publish his work.

From this viewpoint, we may say that the vulcanization reaction proceeds in the following manner.



That is, activated sulfur apparently first adds to the double bonds, forming thioketones, and these in turn group together, forming bridges such as tri-thioethers.

Based on this scheme, aftervulcanization, and the changes in physical properties resulting from it, can be easily explained, and the reaction of vulcanized rubber with hydrazine can be expressed by the following equations.

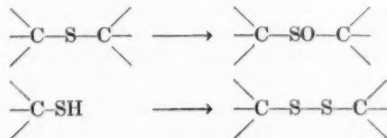


EXPERIMENTAL PART

OXIDATION OF LOW MOLECULAR SULFUR COMPOUNDS

Examples of reaction of $\begin{array}{c} \diagup \text{C}-\text{S}-\text{C} \diagdown \\ | \quad | \end{array}$, $\begin{array}{c} \diagup \text{C}-\text{SH} \diagdown \end{array}$, $\begin{array}{c} \diagup \text{C}-\text{S}-\text{S}-\text{C} \diagdown \\ | \quad | \end{array}$ type of compounds with organic peracids are comparatively numerous¹².

Disregarding compounds of special structure oxidation generally proceeds in the following manner under mild conditions.



Therefore, a mixture of 35 per cent hydrogen peroxide and glacial acetic acid is unable to remove these types of combined sulfur at room temperature as $\text{SO}_4^{''}$.

We have been able to prepare 3,3,5,5-tetraphenyldimethylene 1,2,4-trisulfide in good yield by passing hydrogen chloride and hydrogen sulfide into alcoholic benzophenone⁸. There are reports that it was obtained when thio-benzophenone was left to stand in air¹³. This trisulfide was unaffected by treatment with the oxidizing agent given above, and so was tetraphenylethylene

sulfide. A part of the combined sulfur of polysulfides, such as *p*-tolyl tri- and tetrasulfide or dibenzyl tri- and tetrasulfide, was removed⁵ as SO_4'' . Thiobenzophenone was quantitatively desulfurized⁴ into benzophenone and SO_4'' , and trithioacetone, which is believed to be a polymer of thioacetone, gives sulfoxide⁴. However, it is interesting to note that in the distillate of trithioacetone or trithiomethylethylketone at normal pressure there was a substance which reacted vigorously with the oxidizing agent, giving combined sulfur⁶ as SO_4'' .

Oxidation of Trithioacetone⁴ and Trithiomethylethyl Ketone⁶

The method of Baumann and Fromm¹⁴ was used for the synthesis of trithioacetone. Five grams of this (m.p. 24°C) was added to a mixture of 100 cc. of hydrogen peroxide (35% H_2O_2) and 100 cc. of glacial acetic acid, and more glacial acetic acid was added until the solution became clear. The mixture was left at room temperature for about one week, and a large quantity of water was added. Silky threadlike lustrous crystals gradually formed. These crystals, recrystallized from alcohol, did not give a sharp melting point and decomposed gradually when heated, showing no sharp decomposition point up to over 200°C .

Analysis:

Sample 1.800 mg.	CO_2	2.700 mg.	C	40.93%
	H_2O	1.026 mg.	H	6.34%
Sample 1.630 mg.	SO_4	1.730 mg.	S	35.42%

Calculated for sulfoxide of trithioacetone:

C	40.00%	H	6.66%	S	35.55%
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Combined sulfur was determined by the method of Stragand and Safford¹⁵.

This sulfoxide was converted into sulfone (m.p. 302°C) by treatment with potassium permanganate in glacial acetic acid solution at 100°C .⁶

Trithiomethylethyl ketone was also treated with hydrogen peroxide (35% H_2O_2) and glacial acetic acid at room temperature. This oxidation product ($\text{C}_{12}\text{H}_{24}\text{S}_3\text{O}_3$), when recrystallized from alcohol solution, decomposed at 124°C . When oxidized with a mixture of potassium permanganate and glacial acetic acid, this sulfoxide was converted into the sulfone (m.p. 269°C)⁶.

Oxidation of Thiobenzophenone⁴

We adopted the method of Staudinger and Freudenberger¹³ for the synthesis of thiobenzophenone, which is to treat benzophenone dichloride with alcoholic sodium hydrosulfide.

The thiobenzophenone obtained was light blue and melted at 51°C , becoming dark blue near the melting point. 0.5389 gram was dissolved in 100 cc. of alcohol, was then added gradually to 150 cc. of a mixture of 100 cc. of 25% H_2O_2 and 150 cc. of glacial acetic acid, and if the solution was not clear, alcohol was added. After standing for about a week at room temperature, 300 cc. of distilled water and hydrochloric acid were added, and the mixture was left for a day. The precipitate of benzophenone was filtered, the filtrate and wash liquor were combined, and SO_4'' was determined by addition of 10 per cent barium chloride. A blank test was made because some sulfuric acid is present in the hydrogen peroxide as stabilizer.

Sample 0.5389 g.	BaSO_4	0.8102 g.	(blank 0.1878 g.)
	S eliminated as SO_4''	15.87%	
	Calculated value	16.17%	

The melting point of benzophenone, formed by oxidation, was 48.5° C and showed no depression when mixed with benzophenone prepared differently. When this analysis was made without a solvent, the $\text{SO}_4^{''}$ formed was not quantitative, and some sulfur was formed with benzophenone.

Since a part of the combined sulfur of vulcanized rubber is quantitatively transformed into $\text{SO}_4^{''}$ by oxidation with 35 per cent H_2O_2 in acetic acid, the experiments were carried out analogously to the case of vulcanized rubber.

However, Kitamura¹⁶ reported that thiobenzophenone is easily transformed into benzophenone by 3 per cent hydrogen peroxide containing potassium hydroxide and that the combined sulfur can be quantitatively determined.

Oxidation of Dibenzyl Tetrasulfide⁵

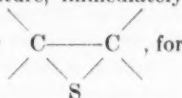
Dibenzyl tetrasulfide (m.p. 53° C) was obtained by the reaction of toluene-thiol and sulfur monochloride. 0.9164 gram was added to 100 cc. of acetic acid, and 100 cc. of 35 per cent H_2O_2 was then added. Since it was insoluble, it was heated for about 10 minutes at 60° C, and the oily mixture was allowed to stand for a week. Then $\text{SO}_4^{''}$ was determined as usual after addition of distilled water and filtration.

Sample 0.9164 g.	BaSO ₄	1.5378 g.	(blank BaSO ₄	0.1320 g.)
	S eliminated as SO ₄ ^{''}		21.07%	

REACTION OF HYDRAZINE WITH LOW-MOLECULAR SULFUR COMPOUNDS

Of the various lower-molecular sulfur compounds, thiobenzophenone polysulfide (tri- or tetra-) and thiol were found to react with hydrazine hydrate (95% $\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$) at ordinary temperature or when heated. As for the thiol, it is believed that hydrazine acts as an oxygen carrier, forming disulfide¹⁷. In the case of the polysulfides, the tri- and tetrasulfides are desulfurized when made to react under heat, forming the disulfide⁵. It is of interest to note that thiobenzophenone reacts with hydrazine at room temperature, immediately

giving hydrazone⁷. On the other hand, additional thioether



example, tetramethylethylene sulfide or tetraphenylethylene sulfide, does not react, even at 100° C.

Reaction of Thiobenzophenone with Hydrazine⁷

When 95 per cent $\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$ was dropped on crystals or into a solution of thiobenzophenone, the latter instantaneously lost its characteristic blue color and hydrazone crystals were formed on standing. After recrystallization from alcohol, the melting point was 98° C, and showed no lowering when mixed with benzophenone hydrazone obtained by synthesis in a different way.

Sample 2.228 mg.	N ₂	0.30 cc.	(29° C/760 mm. Hg)	N:	14.57%
				Calculated	N: 14.29%

When aqueous lead acetate was added to the remaining solution after reaction, lead sulfide was formed.

Hydrazone obtained either from thiobenzophenone or benzophenone is stable and does not form ketoazine at room temperature, even in the presence of excess hydrazine. However, when excess of hydrazine and acetic acid

mixture was dropped into acetophenone at room temperature, ketoazine (m.p. 121° C) was formed immediately, with evolution of gas.¹⁸ This phenomenon is especially intense with aliphatic ketones. Therefore it is easily understandable that, generally, hydrazone transforms into ketoazine.¹⁹

DESULFURIZING REACTION OF THIOMBENZOPHENONE⁸

Thiobenzophenone formed hydrazone when made to react with hydrazine, but in many cases numerous reagents acted as oxygen carriers, giving benzophenone by desulfurization. For example, thiobenzophenone was desulfurized to benzophenone by the action of silver nitrate and mercury, with formation of the corresponding metallic sulfides. The desulfurizing action of alcoholic potash has been already known²⁰, but milk of lime, aqueous ammonia, and sodium sulfite were also effective for benzophenone formation, when heated. Furthermore, alcoholic methyl iodide easily reacted with thiobenzophenone, forming trimethylsulfonium iodide.

Reaction with Mercury

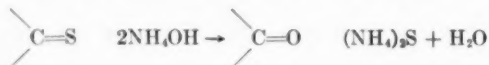
When about 1 gram of mercury was added to 0.2 gram of thiobenzophenone in alcohol and shaken at room temperature, the reaction occurred immediately, with precipitation of black mercury sulfide. However, it took about 140 hours at 10–15° C for the blue color due to the thioketone radical to disappear. Benzophenone was obtained from the alcoholic solution after filtration to remove mercury sulfide. It is believed that mercury acts as an oxygen carrier in this reaction.

Reaction with Silver Nitrate

When 0.5 gram of solid silver nitrate was added to about 0.2 gram of thiobenzophenone in alcohol and shaken at room temperature, a black precipitate was formed. The black precipitate seemed to be Ag₂S, because, when concentrated hydrochloric acid was added and the mixture was warmed with subsequent addition of aqueous sodium arsenite, it turned yellow, giving off hydrogen sulfide. Benzophenone was obtained also from the remaining solution after filtration to remove the black precipitate. However, the nature of the reaction of silver nitrate with thiobenzophenone is not yet clear.

Reaction with Ammonia

No reaction occurred when aqueous ammonia (NH₃ 28%) was added to alcoholic thiobenzophenone at room temperature, but when heated in a sealed tube, benzophenone was formed immediately, with desulfurization. Moreover, since hydrogen sulfide was identified in this solution, which is believed due to ammonium sulfide, the reaction may be shown as follows:

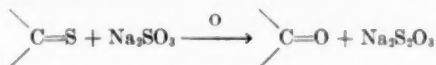


Reaction with Calcium Hydroxide

No reaction by the addition of calcium hydroxide to alcoholic thiobenzophenone at room temperature was observed, but at 40–50° C, desulfurization occurred gradually, with formation of benzophenone.

Reaction with Sodium Sulfite

No reaction occurred when the theoretical amount of solid sodium sulfite was added to alcoholic thiobenzophenone at room temperature, but at 40–50° C, desulfurization was complete within 40 hours, and benzophenone was obtained from the filtrate. The residue formed a white precipitate with silver nitrate, which changed to brown and then to black. Therefore, the reaction with sodium sulfite is as follows:



Reaction with Methyl Iodide

Alcoholic thiobenzophenone, when treated with methyl iodide at room temperature, reacted faster than did the other types of sulfur compounds. When 3 moles of methyl iodide were added to 1 mole of thiobenzophenone and left in a sealed tube at room temperature (20° C), a white precipitate formed within 12 hours, which, recrystallized from water, melted at 203° C. This showed no lowering when mixed with trimethylsulfonium iodide. Benzophenone iodide formed by this reaction was difficult to crystallize and, therefore, was not identified.

REACTIONS WITH THIOBENZOPHENONE

Thiobenzophenone not only gave benzophenone easily when oxidized with nitric acid or potassium permanganate, but also formed benzophenone peroxide dimer²¹ when treated with hydrogen peroxide (35%) and sulfuric acid. This peroxide was also obtained from benzophenone, but it differed from the peroxide previously known²² only in its melting point. Thiobenzophenone was transformed into a polymer with melting point of 146° C by heating with zinc oxide in a sealed tube⁴, and this polymer was formed also when a small amount of ethylenediamine hydrate was dropped into alcoholic thiobenzophenone. However, when excess ethylenediamine hydrate was added at room temperature, desulfurization occurred, giving ethylenediamine, melting at 116° C⁴.

Reaction of Thiobenzophenone with Sulfuric Acid-Hydrogen Peroxide

When alcoholic thiobenzophenone (2 grams) was gradually dropped, with cooling, into a mixture of 100 cc. of 35% H₂O₂ and 100 cc. of concentrated sulfuric acid, the thiobenzophenone immediately lost its characteristic blue color and turned light yellow. After being kept for 4.5 days below 15° C, 500 cc. of water was added and allowed to stand so that most of the crystalline substances agglomerated. The melting point was 70° C when crude crystals obtained by filtration were recrystallized from alcohol. After a week of standing, further crystals were obtained from the filtrate, which made the total yield 1.8 grams.

Analysis:

Sample	CO ₂	H ₂ O	C	H
3.390 mg.	9.690 mg.	1.840 mg.	77.96%	6.07%
3.460 mg.	9.870 mg.	1.830 mg.	77.79%	5.92%
Calculated for	C ₂₄ H ₂₀ O ₄		78.78%	5.05%

The molecular weight by Rast's method, using camphor, was 346, 338; calculated for peroxide (dimer) 396.

This peroxide sublimed, but was comparatively stable, and did not explode when struck. When heated for 5 hours in a sealed tube with dilute sulfuric acid, benzophenone was partly formed, and hydrogen peroxide was identified.

Synthesis of Peroxide (Dimer) from Benzophenone²¹

Marvel and Nichols²² were able to obtain benzophenone peroxide, $C_{26}H_{20}O_4$, with melting points 206.5–207.5° and 214–215.5° C by ozonolysis of the diphenyl compound, but they were not able to obtain peroxides from benzophenone directly by treatment with sulfuric acid-hydrogen peroxide or other peracids.

By the following procedure, we were able to obtain the peroxide (dimer), melting 70° C, from benzophenone (m.p. 48.5° C).

Benzophenone (2 grams) dissolved in acetic acid was added to a mixture of 50 cc. of 35 percent hydrogen peroxide and 20 cc. of concentrated sulfuric acid, kept below 20° C, and more acetic acid added if the solution became turbid. When the solution was poured into 500 cc. of water after being left for a week, an oily reaction product collected on the surface of the liquid. When this stood longer, the oily product was transformed into lustrous needlelike crystals, which diffused into the liquid. The melting point after these were recrystallized from alcohol was 70° C, with no lowering when mixed with the oxidation product obtained from thiobenzophenone, given above.

Formation of Polymer from Thiobenzophenone²³

Thiobenzophenone (0.3 gram) and 0.1 gram of zinc oxide were heated for 3 hours at 150–160° C in a sealed tube, the reaction product was extracted with ether, and was recrystallized from alcohol. The melting point⁴ was 146° C. There is a substance corresponding to this product in the literature²⁴ which is said to be a tetramer of thiobenzophenone. During the determination of the melting point, it gradually began to turn blue, starting around 90° C, showed a sharp melting point at 146° C, and simultaneously became dark blue, and then colorless on cooling.

Analysis:

Sample 0.4372 g.	BaSO ₄	0.5049 g.	S	15.86%
Sample 0.5281 g.	BaSO ₄	0.6238 g.	S	16.23%
Calculated for $(C_{13}H_{10}S)_4$				16.17%

However, with excess zinc oxide, a reaction occurred with zinc sulfide and sulfur, giving benzophenone¹⁸.

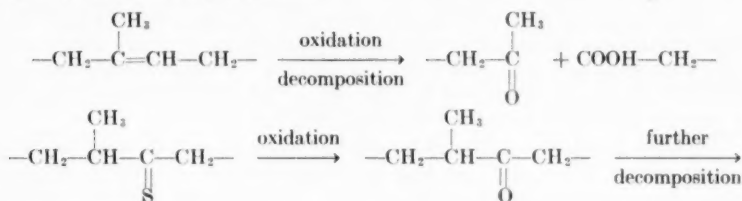
It was possible to determine quantitatively the combined sulfur of this polymer, the original thiobenzophenone, and 3,3,5,5-tetraphenyldimethylene 1,2,4-trisulfide by fusion with a mixture of potassium nitrate and sodium carbonate in a nickel crucible. If the fusion was carried out gradually, tetraphenylethylene (m.p. 222° C) was formed⁸. This polymer with the same melting point of 146° C was formed when ethylenediamine hydrate⁴ or alcoholic sodium hydrosulfide¹⁸ was added to alcoholic thiobenzophenone.

This substance is different from benzohydril disulfide²⁵ (m.p. 153° C).

OXIDATION-DECOMPOSITION OF RAW AND VULCANIZED RUBBER²⁶

It has been reported that when natural rubber is treated with a mixture of acetic acid and hydrogen peroxide it gives alcohol-soluble oxidation products²⁷.

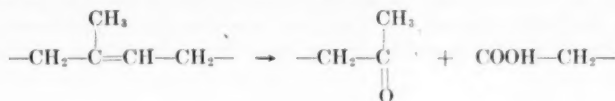
It was found also that this substance was an intensely degraded oxidation product, with ketone or carboxyl radical at the position of scission²⁸. It was observed also that all types of vulcanized rubber, soft and hard, are very easily decomposed into low-molecular compounds by this oxidizing agent. It is natural for the scission of the double bond in soft vulcanized rubber to be analogous to the case of raw rubber, but the interesting point lies in the reaction of ebonite containing about 32 per cent of combined sulfur. Although the double bonds are saturated with sulfur, these ebonites were easily decomposed, and about one-third of the combined sulfur was eliminated quantitatively as SO_4^{--} . The oxidation products of ebonite also contained ketone radicals, and when further oxidation occurred, decomposition proceeded, centering around the ketone radical. Therefore, oxidation decomposition may be shown by the following equation.



Oxidation Decomposition of Natural Rubber²⁸

Purified natural raw rubber (32 grams), cut into small pieces, was immersed in a mixture of 200 cc. of hydrogen peroxide (35% H_2O_2) and 400 cc. of glacial acetic acid and left at room temperature (20–22° C) for 10 days. During this period the rubber was decomposed by oxidation and dissolved. When this solution was poured into 7 liters of an aqueous solution containing 400 grams of sodium carbonate, white amorphous substances coagulated. This product was left to stand for a few days, then washed and dried. The dried product weighed 33 grams, but the rest of the reaction product, about 12–13 grams by calculation, was soluble in water and remained in solution. The amorphous product was dissolved in alcohol and purified by precipitation. It then gave on analysis: C 65.53%, H 9.12%. When 3 grams of the purified oxidation product was boiled in an aqueous solution of 3 grams of potassium hydroxide, alkali soap soluble in water was formed. When hydrochloric acid was added to aqueous solutions of the sodium or potassium salt, white amorphous substances coagulated again, and with alcoholic 2,4-dinitrophenylhydrazine sulfate, the hydrazone was formed from this alcoholic solution of this coagulum. The hydrazone was a yellow powder containing 7–8.5 per cent nitrogen. On the other hand, when excess 95 per cent alcoholic hydrazine hydrate was added to the alcoholic oxidation product, the mixture heated to dryness on a bath, and reprecipitated from alcohol, a powder containing 8–10 per cent nitrogen was obtained.

From these experiments, it is believed that scission of natural rubber by the oxidizing agent proceeds in the following manner.



Furthermore, from calculation of the percentage of nitrogen contained in the 2,4-dinitrophenyl hydrazone of the oxidation product, the average molecular weight of the oxidation product, thus obtained, corresponds to about $C_{25} \sim C_{30}$. Therefore, on further consideration of the analytical value of C 65.53% and H 9.12%, the double bonds which did not take part in the scission of the molecules seem to be saturated with polar radicals, such as the hydroxyl radical.

Oxidation Decomposition of Soft Vulcanized Rubber²⁸

The samples in these experiments were vulcanized soft rubber, composed of only the so-called "rubber and its combined sulfur", which had been prepared by curing a pure rubber-sulfur mix, followed by extraction with acetone to remove free sulfur and other impurities. Standard smoked sheet (100 grams) and 15 grams of sulfur were mixed on a roll mill, then cured for 1 hour at 144° C in a press, and cut into very small pieces after standing for a week. Five grams of each was taken and extracted continuously for 50 hours with acetone at the extraction rate of a cycle every 3.5 minutes. Various experiments were performed on samples prepared in this way. The combined sulfur was 3.92 per cent by nitric acid-bromine treatment, followed by fusion.

Oxidation products.—Acetone-extracted samples (5 grams) were immersed in a mixture of 100 cc. of 35 per cent hydrogen peroxide and 100 cc. of glacial acetic acid at room temperature (10–15° C). In a week the rubber completely dissolved, giving a clear solution. The decomposition proceeded much faster than when natural raw rubber was oxidized. When the oxidation products were treated as was raw rubber, a white amorphous powder was obtained. The powder obtained after purification by reprecipitation from alcohol contained 1.17 per cent of combined sulfur. This value has no quantitative significance, but it shows that there is sulfur firmly combined with the rubber which remained in the oxidation products, even after oxidation. The nitrogen content was 8.72 per cent for the yellow 2,4-dinitrophenyl hydrazone derived from the purified white amorphous powder.

Determination of Combined Sulfur Forming $SO_4^{''}$ on Oxidation

To 3 grams of homogeneously mixed acetone-extracted pieces of sample in a 500 cc. beaker, 100 cc. of 35 per cent H_2O_2 and 100 cc. of glacial acetic acid were added, and comparative determinations were made of the combined sulfur eliminated as $SO_4^{''}$ after standing for different times. A blank test was also performed. It took about 5 days for the rubber to dissolve completely to a clear solution at room temperature (10–15° C), but at higher temperatures (40–50° C), the time was much shorter. To the clear solution, 200 cc. of distilled water, and some hydrochloric acid were added, the mixture was allowed to stand for 24 hours, the white amorphous powder formed was filtered, and the filtrate and the washing were combined and made up to about 500 cc. If this solution became turbid, 2–3 cc. more of hydrochloric acid was added, and, after standing, filtration was repeated. The quantitative determination of $SO_4^{''}$ was made in the usual way, using 10 per cent aqueous barium chloride, and weighing the $BaSO_4$ formed. A blank test was also made, which gave 0.1206 gram of $BaSO_4$ for 100 cc. of hydrogen peroxide. The results obtained were as follows:

COMBINED SULFUR ELIMINATED AS $\text{SO}_4^{''}$ BY OXIDATION

Sample (g.)	Reaction time (days)	BaSO_4 (g.)	S (%)
3.2403	7	0.3038	1.29
3.2002	10	0.3133	1.35
3.1905	20	0.3081	1.32

Out of the 3.92 per cent of total combined sulfur in the sample, it may be concluded from these results that 1.3 per cent of combined sulfur was of the type removable by oxidation; the rest remained in the oxidation products. It is believed that the latter type remained perhaps as sulfoxides.

Oxidation Decomposition of Ebonite²⁹

Standard smoked sheet (100 grams) was mixed with 60 grams of sulfur on a roll mill and cured for 6 hours at $150 \pm 5^\circ \text{C}$ in an autoclave. Five grams each of very finely divided vulcanizate was extracted with acetone for 100 hours, with the extraction rate of a cycle every 4.5 minutes. The ebonite powder after this extraction contained about 32 per cent of combined sulfur.

Oxidation decomposition of ebonite.—Acetone-extracted ebonite powder, thus obtained, was immersed in a mixture of 100 cc. of 35 per cent hydrogen peroxide and 100 cc. of glacial acetic acid, and kept at room temperature ($15\text{--}20^\circ \text{C}$). The reaction was much faster than in the case of raw rubber or soft vulcanized rubber, and the sample dissolved completely in about 3 days. After standing for a week, a large quantity of water was added, but no coagulation occurred. Therefore, excess aqueous barium chloride was added, and part of the decomposition products were coagulated with the barium sulfate formed. After filtration, the residue was extracted with alcohol, and a red precipitate of hydrazone was formed immediately when aqueous 2,4-dinitrophenyl hydrazine sulfate was added. This precipitate was collected and analyzed after reprecipitation from alcohol.

Analysis:

Sample 2.080 mg.	CO_2	3.725 mg.	H_2O	1.185 mg.
	C:	48.87%	H:	6.37%
Sample 2.950 mg.	N_2	0.208 cc.	(767.2 mm. Hg/ 17°C)	
	N:	8.21%		
Sample 1.870 mg.	SO_4	0.510 mg.	S:	9.10%
1.930 mg.		0.550 mg.		9.51%

Combined sulfur was also determined by the method of Stragand and Safford¹⁸.

When the ebonite powder was immersed in a mixture of 35 per cent hydrogen peroxide and sulfuric acid, a very vigorous reaction occurred. A water-soluble calcium salt formed when the reaction was cautiously controlled by cooling and stirring until the ebonite powder decomposed completely and was then neutralized with lime. The existence of the ketone group was not observed in the free acid reconverted from this calcium salt by acid treatment or in the mixture of the oxidation products obtained by molecular distillation of the ester formed from this salt. It is, therefore, believed that the oxidation decomposition of ebonite is due to the thioketone radical.

Determination of combined sulfur eliminated as $\text{SO}_4^{''}$ by oxidation.—The acetone-extracted ebonite powder was subjected to oxidation-decomposition in a mixture of 35 per cent H_2O_2 and glacial acetic acid, and the combined sulfur eliminated as $\text{SO}_4^{''}$ was determined.

COMBINED SULFUR ELIMINATED AS SO_4'' BY OXIDATION

	I	II	III	IV
Sample (g.)	3.0000	2.000	2.4854	3.0000
35% H_2O_2 (cc.)	100	150	100	150
CH_3COOH (cc.)	100	100	150	150
Oxidation temperature ($^\circ\text{C}$)	20-22	14-15	30-35	30-35
Reaction time (days)	7	8	5	4
BaSO_4^* (g.)	2.3031	1.5114	1.9392	2.3261
S (%)	10.5 ₅	10.3 ₅	10.7 ₂	10.6 ₅

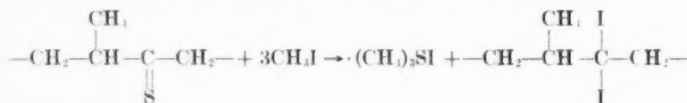
* Corrections were made for H_2SO_4 in the hydrogen peroxide.

When excess aqueous barium chloride was added (although it was inconvenient, since a part of the oxidation product precipitated with barium sulfate), it did not affect the determination.

Reaction of ebonite with methyl iodide.—Meyer and Hohenemser²⁹ were the first to treat vulcanized rubber with methyl iodide to study the structure of vulcanized rubber, and by a comparison with low-molecular sulfur-containing compounds, they believed that the existence of thioether was proved. Later, besides the studies of Brown and Hauser³⁰, a comprehensive paper was published by Selker and Kemp³¹.

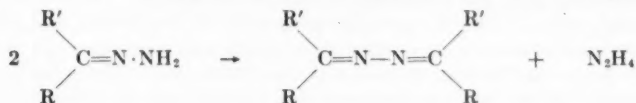
It is interesting that Selker and Kemp found that especially, when ebonites of natural rubber and GR-S were treated with methyl iodide at 24°C , one-third of the combined sulfur was eliminated as $(\text{CH}_3)_3\text{SI}$, whereas two-thirds remained combined with the rubber. If we compare this fact with that which we observed, that is, that about one-third of the total combined sulfur is eliminated as SO_4'' when oxidized with a mixture of acetic acid and hydrogen peroxide, it seems that the light to unveil the mystery of rubber vulcanization has come into view.

We also obtained trimethylsulfonium iodide, with melting point 203°C , and ebonite-iodide by the reaction of methyl iodide and acetone-extracted ebonite powder. However, the ebonite-iodide did not decompose by oxidation when immersed in acetic acid-hydrogen peroxide mixture²⁹. There were no changes even after being immersed for about a year, or when the concentration and temperature of the oxidizing agent were altered. This is a very interesting phenomenon, for it shows that ebonite-iodide is different in structure from the original ebonite, and to explain this phenomenon it seems that thioketone in ebonite reacts specifically with methyl iodide and loses combined sulfur as $(\text{CH}_3)_3\text{SI}$, which is replaced by iodine. As with low-molecular sulfur-containing compounds, we have shown that thiobenzophenone reacts vigorously with methyl iodide, giving $(\text{CH}_3)_3\text{SI}$ and benzophenone iodide, which we believe supports the following view of the reaction of ebonite.

REACTION OF VULCANIZED RUBBER AND HYDRAZINE³²

It has been shown that, with hydrazine, thiobenzophenone is easily converted into hydrazone, which is relatively stable and does not change into the corresponding ketoazine at room temperature. Reports on the formation of

ketoazine from hydrazines are comparatively numerous for aliphatic compounds¹⁹. It is believed that a ketoazine is formed from 2 moles of hydrazones.



For example, the hydrazone of acetone changes gradually into the corresponding ketoazine when stored, and the hydrazone of methylethyl ketone easily forms the ketoazine at room temperature. Since almost all propyl ketone is converted into ketoazine during its synthesis, isolation of the hydrazone is difficult¹⁹. This shows that, in the equation given above, as the asymmetry of R and R' increases, formation of the ketoazine becomes easier, and the following phenomenon was also observed in our experiments¹⁸. Benzophenone, even in the presence of excess hydrazine, did not react, but when acetic acid was added and the mixture was kept for 24 hours at room temperature, the ketoazine was formed. However, acetophenone and its derivatives reacted with hydrazine hydrate alone at room temperature, forming their ketoazines. Therefore, it is necessary to observe the reaction of hydrazine with thioketone from this point of view. Generally it is believed that a hydrazone is transformed into the ketoazine with the exception of compounds of special structure. In particular, when the structure of rubber is considered, the following experimental results may be easily understood.

Reaction of Soft Vulcanized Rubber with Hydrazine²³

To investigate whether a new nitrogen network is formed when soft vulcanized rubber samples are treated with hydrazine, the amount of nitrogen combined, and also the changes in physical properties, were determined.

The so-called "rubber and combined sulfur" samples for the experiments were prepared in the following manner. Standard smoked sheet (100 grams) and 10 grams of sulfur were mixed, and cured for 30 minutes at 147° C in a press, the vulcanizate was cut into very small pieces, and each 5 grams was extracted continuously with acetone for 100 hours at the rate of a cycle every 2.5 minutes. On analysis of this extracted sample, the total combined sulfur was 1.38 per cent, and the combined sulfur removable by oxidation was 0.78 per cent.

These test-pieces were heated with 95 per cent hydrazine hydrate for 30 minutes in a sealed tube, and then immersed in a large volume of water (the water being changed frequently), and then washed for 5 hours with heating to remove excess hydrazine. After being dried, microanalyses for nitrogen were made. Blank tests of untreated samples were also made, and the corrected nitrogen content was found to be 0.28–0.42 per cent, showing that vulcanized rubber treated with hydrazine hydrate contained combined nitrogen. Furthermore, it was possible to detect hydrogen sulfide in the aqueous solution obtained by diluting the hydrazine hydrate used in the treatment by the addition of aqueous lead acetate.

Changes in Modulus of Vulcanized Rubber Treated with Hydrazine

It was observed that when the samples of soft vulcanized rubber, after immersion in concentrated hydrazine hydrate at room temperature for a definite time, were allowed to stand in open air, the modulus and tensile strength gradu-

ally increased. These phenomena were very intense and unequalled in the case of untreated vulcanized rubber. The increase in elongation was particularly interesting from the standpoint of rubber elasticity.

As given above, when the so-called sample of "rubber and combined sulfur only" was used in these experiments, these tendencies were observed in a short period of time, but the phenomenon was also observable with rubber products, for example, rubber vulcanizates containing accelerators and zinc oxide. For industrial purposes, however, it is desirable to apply the treatment to thin rubber sheets.

Vulcanized rubber sample.—A mix of smoked sheet rubber (100 grams) and 9 grams of sulfur was cured for 1 hour at 147° C in a press, kept for a month in darkness, and 30 rectangular test-pieces 6 cm. long were prepared. These test-pieces, carefully placed in Soxhlet extractors, were extracted with acetone

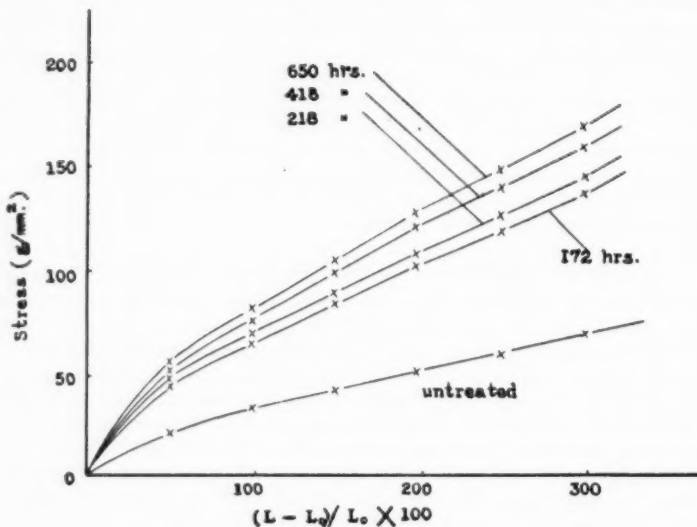


FIG. 1.—Stress-strain relations of rubber treated with hydrazine.

continuously for 28 hours at the extraction rate of a cycle per 3.5 minutes. The test-pieces were inverted after the first 14 hours' extraction, and care was taken that the pieces did not adhere to each other or become strained during the extraction. This procedure was insufficient to remove all of the free sulfur and other impurities in the rubber, but it was sufficient to trace the changes in physical properties after treatment with hydrazine. Each of the 30 test-pieces were cut in halves, making a total of 60, and all acetone was eliminated in a vacuum drier. Ten pieces, picked at random, were tested for stress-strain properties with a small Schopper tensile tester, with a pull velocity of 1 cm. per 15 seconds at room temperature (14° C), and distance between marks of 1.0 cm. The average thickness and width were 1.5 mm. and 5.3 mm., respectively. After testing, these samples were cut into small pieces and immediately oxidized

with a mixture of 35 per cent hydrogen peroxide and glacial acetic acid. They contained 0.92 per cent of combined sulfur removable as $\text{SO}_4^{''}$.

Hydrazine hydrate treatment.—Forty test-pieces were immersed in 95 per cent hydrazine hydrate for 25 days at room temperature. During this period the surface of the samples gradually became green and dark green when taken out, but when washed and allowed to stand, the color disappeared and the samples finally became transparent. When observed by transmitted sunlight, stripes were observable while the hydrazine was still absorbed in the rubber, but this too disappeared with time.

Tracing changes in modulus.—Hydrazine-treated test-pieces were allowed to stand for 172, 218, 418, and 650 hours at room temperature, and were tested for their modulus values under the same conditions as was the untreated sample. Averages of ten pieces each were taken for the values of the moduli at elongations of 200 and 400 per cent.

Elongation $\frac{l-l_0}{l_0} \times 100$	Untreated	Modulus (grams per sq. mm.) Time of standing after treatment (hours)			
		172	218	418	650
200	48.8	98.8	105.5	119.5	124.4
400	67.1	136.0	144.5	161.0	167.1

Their changes of stress-strain properties are shown graphically in Figure 1.

Changes of Tensile Strength and Elongation of Vulcanized Rubber Treated with Hydrazine³⁴

Masticated standard smoke sheet (500 grams) was divided into 100-gram samples, which were further mixed with 3, 6, 9, 12, and 15 grams of sulfur, respectively, and each batch was cured for 1 hour at 147° C in a press. Care was taken to prepare these samples under the same conditions. Small size dumbbell test-pieces were prepared, each 0.16 ± 0.01 cm. thick, 0.5 cm. wide, and 3 cm. long.

Ten pieces were extracted with acetone continuously for 50 hours, with the extraction rate of a cycle per 3.5 minutes, and divided into two groups, each of five pieces, out of which, one group after treatment with 95 per cent hydrazine hydrate for 2 weeks at room temperature was allowed to stand for 45 days, while the other half was untreated.

On the other hand, finely cut samples, each 8 grams, were extracted with acetone continuously for 102 hours, and the total combined sulfur and combined sulfur removable as $\text{SO}_4^{''}$ by oxidation were determined.

Results of the analyses.—

Parts of sulfur per 100 parts of rubber	Total combined sulfur (%)	Combined sulfur removable as $\text{SO}_4^{''}$ (%)
3	0.94	0.37
6	1.63	0.58
9	2.59	1.02
12	3.47	1.30
15	4.01	1.55

Physical test results.—The pull velocity was 1 cm. per 20 seconds; the temperature was 17° C.

Parts of sulfur per 10 parts of rubber	Before hydrazine treatment			After hydrazine treatment		
	Modulus* (g./mm. ²)	Tensile strength (kg./cm. ²)	Elongation at break (%)	Modulus* (g./mm. ²)	Tensile strength (kg./cm. ²)	Elongation at break (%)
3	9.7	8	—	—	35	—
6	24.9	15	600	52.7	58	850
9	45.2	33	700	148.9	89	950
12	74.8	30	—	203.4	72	—
15	87.6	27	—	152.8	53	—

* Modulus at 200% elongation.

When the samples were treated with hydrazine, not only the modulus, but also the tensile strength and elongation increased considerably. However, in the case of rubber which had been considerably overcured, although some combined sulfur was removable by oxidation (the thioketone type), this effect was slight. In these samples, since the degree of network was already dense, it is believed that further formation of the new network was difficult. The tendency for the elongation to increase by hydrazine treatment shows that the free ends of the molecules to which other ends are already bound to the network were susceptible to cross-linking. Moreover, when the difference of total combined sulfur and the thioketone type of combined sulfur is taken as the bridge-type of combined sulfur is plotted against the modulus, a smooth curve is obtained, making possible a theoretical explanation of rubber elasticity³⁴.

Swelling Hydrazine-Treated Rubber³⁵

According to Flory and Rehner³⁵, theoretical relations exist not only between network concentration and elasticity, but also between the former and swelling properties.

To determine whether a new network is formed by hydrazine treatment, experiments on swelling were carried out.

Sulfur (9 grams) was mixed into 100 grams of smoked sheet rubber in 5 minutes, masticated for 25 minutes, and cured for 1 hour at 147° C. Small rectangular test-pieces extracted with acetone continuously for 50 hours were divided into two groups. One group, after being immersed in 95 per cent hydrazine hydrate for 15 days at 20° C, was taken out, and left for 45 days in a room, while the other group was kept for 60 days in a dark room. The results for modulus at 200 per cent elongation and swelling in benzene, which were determined under the same conditions simultaneously, are given in the next table. V_0 and V are the volumes before and after swelling, respectively.

	Modulus (g./mm. ²)	Swelling index ($V/V_0 \times 100$) (%)
Untreated (kept in darkness)	52.1	764.5
Hydrazine-treated	112.5	491.3

These results also show that new cross-linking by ketoazine occurs.

Comparison of Hydrazine Treatment and Ammonia Treatment of Vulcanized Rubber⁸

Since the reaction of thioketone with hydrazine forms the hydrazone, with subsequent formation of ketoazine, it is likely that because thioketone is present in vulcanizates, this same effect as by hydrazine treatment occurs.

However, like ammonia, hydrazine acts as an oxygen carrier, causing thiols to form disulfides. Therefore, if thiols are present in vulcanizates, increase of cross-linkages by hydrazine treatment does not prove definitely the presence of thioketone. However, since, unlike hydrazine, ammonia acts as a desulfurizing agent, causing a thioketone to form a ketone, if the physical properties of vulcanized rubber are unaffected or are impaired to some extent by ammonia treatment, the presence of a thiol type of sulfur in vulcanizates is not expected. Actually when vulcanized rubber was treated with both of these reagents and its modulus tested after a definite period, hydrazine-treated rubber showed considerably improved physical properties, but on the other hand, ammonia-treated rubber was much inferior in properties to the original samples.

A mixture of 100 grams of standard smoked sheet and 10 grams of sulfur was cured for 45 minutes at 147° C. Small rectangular pieces of this vulcanizate were extracted with acetone continuously for 92 hours, and divided into three groups. One group was immersed in a mixture of 29 per cent ammonia and alcohol for 160 hours at room temperature, then heated for 30 hours at 40–50° C, with care being taken to add more aqueous ammonia several times because of evaporation, and finally taken out and allowed to stand for 32 days. Another group was treated with 28 per cent aqueous hydrazine under the same conditions. The third untreated group was kept in darkness for comparison. As will be shown below, because of aftervulcanization (after-cross-linking) caused by thioketone, although the vulcanized rubber was composed of rubber and combined sulfur only, the modulus increased slightly on standing. Therefore, it is most suitable for comparison with ammonia-treated samples.

The test-specimens were 0.2 cm. thick, 0.4 cm. wide, and 3.5 cm. long, and the distance between markings was 1 cm. Measurements were made with a small size Schopper tester with pull velocity of 1 cm. per 30 seconds at room temperature (15° C).

α	$\alpha = \frac{1}{\alpha^2}$	Stress (g. per sq. mm.)		
		Ammonia-treated	Hydrazine-treated	Untreated
2	1.750	37.5	55.6	43.7
3	2.880	57.2	85.6	68.7
4	3.938	76.2	112.0	95.0
5	4.960	—	151.0	114.0

α is the ratio of elongation at the corresponding stress to the original length. When short rectangular test-pieces were used, only ammonia-treated rubber ruptured before reaching 400 per cent elongation. The result is shown graphically in Figure 2.

From these experiments, the presence of the —SH radical in vulcanized rubber cannot be expected, and since it has long been known that, in vulcanizing a pure rubber-sulfur mixture, an atom of sulfur combines for every double bond which is lost³⁶, a polysulfide, for example, of the —S—S—S— or —S—S—S—S— type, cannot be expected. Therefore in the case of vulcanizates of only "rubber and its combined sulfur", our supposition that the combined sulfur which is removable by oxidation is the thioketone type alone, and that it forms a new ketoazine cross-linkage by reaction with hydrazine seems to be valid. Of course, if the thioketone molecules in rubber exist in a state where they are isolated from each other without any opportunity to collide, this phenomenon may not occur, but if the reaction of rubber and sulfur proceeds as chain reactions in parts, the formation of ketoazine bridges can be easily understood, and the explanation of the changes in physical properties by aftervulcanization

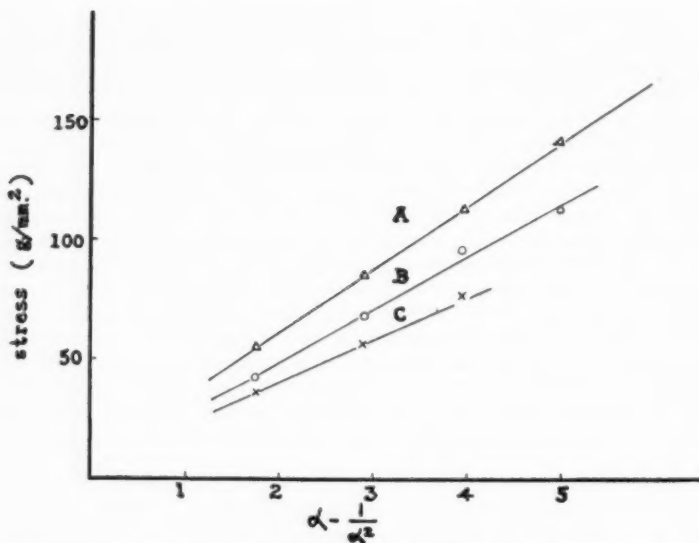


FIG. 2.—Comparison of soft vulcanized rubber treated with hydrazine and with ammonia, respectively.

or overvulcanization becomes possible. Especially, the postulation that heterogeneous vulcanization reaction occurs and that cross-linked sulfur finally forms localized heterogeneous groupings may be assumed, as was stressed by Williams³⁷.

CROSS-LINKING BY THE TRANSFORMATION OF THIOKETONE³⁸

When vulcanizates consisting of natural rubber and sulfur alone were extracted with acetone until the remaining acetone extractable portion became insignificant and then were heated at a definite constant temperature or were kept for a long period at room temperature, the thioketone type of combined sulfur gradually decreased. This tendency was the same when acetone-extracted ebonite was heated. When the extraction of free sulfur was insufficient, this tendency to decrease was not uniform, and the change in the amount of the thioketone type of sulfur with time formed a zigzag curve. This is due to after-vulcanization caused by the remaining free sulfur. Therefore, from this phenomenon, conversely, it is possible to evaluate the acetone extraction procedure.

Heat Treatment of Acetone-Extracted Soft Vulcanized Rubber

Standard smoked sheet (100 grams) was masticated and mixed with 18 grams of sulfur in 50 minutes, and the mixture was cured in a press for 1 hour at 147° C. Ten-gram samples of very finely cut pieces of this product were extracted with acetone for 114 hours at a rate of a cycle per 2.5 minutes. The combined sulfur after extraction was 3.92 per cent. Then 3–4 grams of each was accurately weighed into a previously weighed Petri dish, and 18 of these were further divided into two groups, out of which one group was placed in an air drying oven at $100 \pm 2^\circ \text{C}$, the other at $150 \pm 2^\circ \text{C}$. Three samples were taken out at definite intervals and subjected to oxidation decomposition by

immersion in acetic acid-hydrogen peroxide, and the average combined sulfur eliminated as $\text{SO}_4^{''}$ was determined each time.

CHANGES IN THE PERCENTAGE OF THIOKETONE TYPE
OF COMBINED SULFUR BY HEATING

Time heated (min.)	0	30	60	90	120	180
$100 \pm 2^\circ \text{C}$	1.25	—	1.19	—	1.13	1.09
$150 \pm 2^\circ \text{C}$	1.25	0.53	0.37	—	—	—

Storage of Acetone-Extracted Vulcanized Soft Rubber at Room Temperature

A pure rubber-sulfur mix of 100 grams of standard smoked sheet and 30 grams of sulfur was prepared as above, and the acetone-extracted samples were placed in accurately weighed Petri dishes without covers, and left in the south side of the room. The period of standing was from summer to autumn, and they were exposed to sunlight through the window glass when the weather was clear. The maximum temperature was 32°C , the minimum 21°C . At definite intervals samples were taken for determinations of the thioketone type of combined sulfur, the original weight being used in the determination, since the weight of the sample increased as oxygen was absorbed, besides dust which might have dropped in.

The averages of two determinations of combined sulfur removable as $\text{SO}_4^{''}$ at definite intervals were as follows.

Period of standing (hours)	Thioketone type of sulfur (per cent)
0	1.93 ₃
408	1.87 ₂
768	1.74 ₆
1158	1.73 ₆

Changes of the Amount of Thioketone Type of Sulfur in Ebonite

Standard smoked sheet (100 grams) was mixed with 60 grams of sulfur and one-half of the mixture was cured at $140 \pm 5^\circ \text{C}$ for 8 hours; the other half at $150 \pm 5^\circ \text{C}$ for 6 hours in an autoclave. The products were then pulverized, and 5 grams of each was extracted with acetone continuously for 100 hours at the extraction rate of a cycle per 4.5 minutes.

After being thoroughly mixed, 2 grams of each of the extracted samples was accurately weighed into a small Petri dish, and these were placed in an air drying oven at $150 \pm 2^\circ \text{C}$. At definite intervals the thioketone type of combined sulfur was determined by immersing the samples, together with the Petri dish, in a mixture of 100 cc. of 35 per cent hydrogen peroxide and 100 cc. of glacial acetic acid for 5 days at room temperature (20 – 22°C). The results of the determinations are given in the following table, in which the percentages of sulfur were corrected for blank tests.

Time heated (min.)	Thioketone type of combined sulfur (per cent)	
	$150 \pm 5^\circ \text{C}$ cure	$140 \pm 5^\circ \text{C}$ cure
0	10.38	11.40
60	9.56	10.53
120	9.04	9.77
180	8.35	—

SUMMARY

In this study much information about the method of distinguishing the state in which sulfur is combined in simple organic compounds consisting of carbon, hydrogen, and sulfur was obtained, and a new theory of vulcanization was postulated as a result of its application to vulcanized rubber.

When activated sulfur reacts with rubber, it first adds to the double bonds, forming thioketones, which in turn, as a characteristic of these radicals, combine with each other, with the formation of a thioether structure.

This transformation of thioketone into thioether takes place, not only during vulcanization, but also gradually after vulcanization.

Because of the presence of thioketone, treatment of vulcanized rubber with hydrazine, forms a new network, that is, a ketoazine cross-linkage.

Combined sulfur of the thioketone type was determined by an oxidizing agent, and as the difference of this value and total combined sulfur a method of determining bridge type of combined sulfur has been proposed. By this method, it was found that, even in ebonite, about one-third of the combined sulfur is the thioketone type, and that the bridge type is only about two-thirds of the total.

The thioketone type of combined sulfur in soft vulcanized rubber is transformed gradually into the thioether type of cross-linkage when allowed to stand at room temperature, and this transformation is accelerated when the temperature is raised. In the case of hard rubber, this phenomenon is also observable, but the rate of this transformation is much slower compared to the former. This tendency is the same in the case of ketoazine cross-linking when rubber vulcanizates are treated with hydrazine.

From these facts, it seems that the distribution of the thioketone radicals is not uniform, and the magnitude of the probability for collision of these radicals to form cross-linkages has a great influence on the properties of rubber after vulcanization. That is, the property of the vulcanizate is greatly affected by the fact whether the thioketone radicals in the vulcanizates are comparatively uniformly distributed or whether they exist in sectional groups or in colonies.

The authors are the first to advance this postulate concerning the chemical structure of vulcanized rubber and its transformation. We believe that when the study is extended, using this postulation, problems such as aging and the differences in the properties of vulcanized rubber accelerated with various accelerators will become clear. Moreover, we believe that it will be of interest to physicists studying rubber elasticity to suggest this idea of colony of cross-linkages. We are now carrying on researches on these problems, and we shall report on them later.

ACKNOWLEDGMENT

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DIFFUSION OF OXYGEN AND OXIDATION OF RUBBERS IN THE PRESENCE OF PHENYL- β -NAPHTHYLAMINE *

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We know now that the oxidation of rubbers takes place in the absence as well as the presence of antioxidants. However, the mechanism and the rate of the free and inhibited processes are altogether different¹. In the presence of a sufficient quantity of a good antioxidant² ("true inhibited oxidation"), oxygen takes part almost exclusively in the immediate process of oxidation of the rubber, while the developing active centers are deactivated by reacting with the antioxidant¹. During free autocatalytic accelerated oxidation, the oxygen takes part in various processes; it initiates a chain process in which it takes part, and also causes many secondary reactions, including most of those which cause rupture of the reactive chains.

In this article we shall discuss only true inhibited oxidation, which is especially important from the practical viewpoint³.

The rate of the process W_i is expressed by the equation:

$$W_i = K_i[P][O_2]\gamma_i \dots \dots \dots (1)$$

where K_i is the constant of the rate of initiation; $[P]$ is the concentration of molecular chain particles in one aliphatic double bond; $[O_2]$ is the concentration of oxygen dissolved in the solution; γ_i is the length of a reactive chain (without side chains)⁴.

We showed that during the oxidation of thin sheets of rubber (30–40 μ) under constant partial pressure of oxygen, W_i is constant (see Figure 1). With a change of the partial pressure of oxygen, this quantity does not change

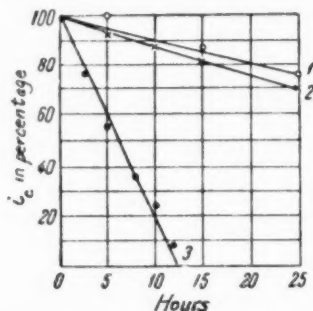


Fig. 1.—Kinetics of consumption of phenyl- β -naphthylamine during the oxidation of rubber at different partial pressures, PO_2 , or oxygen. 1. $PO_2 = 10$ mm. mercury. 2. $PO_2 = 20$ mm. mercury. 3. $PO_2 = 760$ mm. mercury. i = remaining free inhibitor (percentage of original quantity).

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the Reports of the Academy of Sciences of the USSR, Vol. 79, No. 3, pages 467–470 (1951).

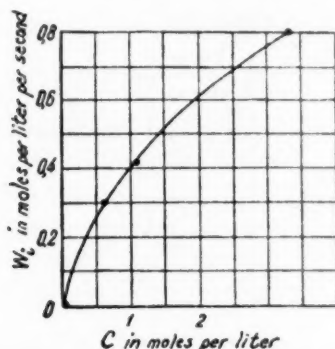


FIG. 2.—Rate of inhibited oxidation of rubber as a function of the partial pressure of oxygen. W_i = rate of oxidation in mole-liters per second. C = concentration of oxygen dissolved in rubber, in moles per liter.

linearly, but according to a curvilinear relation (see Figure 2), expressed approximately by the equation:

$$W_i = K_1[P]^x[O_2]^y = K_1[O_2]^1 \dots \dots \dots (2)$$

This equation shows that, with a decrease of the concentration of oxygen in solution, the number of successive polymerizations increases, i.e., the length of a chain increases. This phenomenon is evidently related to the different activity of the oxygen and hydrogen radicals with respect to the inhibitor.

Since rubber reacts with oxygen which has diffused in it, the rates of oxidation and diffusion are related by the Fick equation (for a single process):

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} + W_i \dots \dots \dots (3)$$

where D is the coefficient of diffusion; C is the concentration of oxygen in the rubber (that is, $C = [O_2]$); x is the distance from the center of the sheet, and $W_i = f(C)$.

In general, it is necessary to know the coefficient of diffusion in the original and oxidized rubbers and the relation of W_i to C . For the case of inhibited oxidation, the value of D can be considered constant, since here the structural changes in the rubber are negligible. We calculated this value according to the Dynes method, based on the study of the variable diffusion process. An investigation of the solubility and diffusion of oxygen in sodium-butadiene rubber was described earlier⁵.

The complete solution of Equation (3) encounters many difficulties because the right side of the equation is not linear.

An approximate linear equation was used:

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} + K_2 C \dots \dots \dots (4)$$

in which the rate of oxidation is a linear function of the concentration of oxygen. The value K_2 is found from the condition according to which the algebraic sum of the deviation of the approximate rate $K_2 C$ from the true $K_1 \sqrt{C}$ in the concentration range from 0 to C equals zero.

We obtain for oxidation at 120° C:

$$K_2 = 4/3K_1 \frac{1}{\sqrt{C}} = 8.15 \times 10^{-5} \text{ sec.}^{-1}$$

The solution of Equation (4) is given by the equation⁶:

$$C(x, t) = C_0 \left\{ \frac{ch\sqrt{K_1/D} \cdot x}{ch\sqrt{K_1/D} \cdot l/2} - \sum (-l)^{n+1} \frac{4(2n-1)\pi}{(2n-1)^2\pi^2 \frac{K_1}{D} l^2} \cos \frac{(2n-1)}{l} K_1 x e^{-\left[K_1 + \frac{D(2n-1)^2\pi^2}{l^2} t\right]} \right\} \dots (5)$$

where C_0 is the solubility of oxygen, $x = \pm l/2$, and l is the thickness of the sheet.

Table 1 gives the distribution of the concentrations of oxygen in rubber during oxidation at 120° C. It is apparent from the table that, for a sheet of rubber

TABLE 1
DISTRIBUTION OF OXYGEN CONCENTRATIONS IN SHEET OF SODIUM-BUTADIENE RUBBER DURING OXIDATION IN THE PRESENCE OF PHENYL- β -NAPHTHYLAMINE (TEMPERATURE, 102° C; OXYGEN PRESSURE, 750 MM. HG)

Total thickness of sheet (mm.)	Time from beginning of oxidation	Form of relation between rate of oxidation and concentration	Distance from middle of sheet as fraction of the total thickness				
			0.500	0.375	0.250	0.125	0.00
1.0	1.0	$W = K_2 C$	1.0	0.766	0.595	0.486	0.448
	2.5		1.0	0.845	0.740	0.675	0.658
	5.0		1.0	0.856	0.699	0.699	0.681
	7.5 and more		1.0	0.856	0.762	0.700	0.682
	Stationary distribution	$W = K_1 \sqrt{C}$	1.0	0.865	0.787	0.731	0.712
1.0	Stationary distribution	$W = K_2 C$	1.0	0.998	0.996	0.996	0.995

* Oxygen concentration on rubber-gas surface was assumed to be unity.

of 1 cm. thickness, oxidized on both sides for 14 hours (5×10^4 sec.), the distribution of oxygen concentrations with respect to thickness becomes practically fixed (see Figure 3).

For a layer of thickness 0.1 cm., the distribution of the concentration becomes fixed after 10–15 minutes. A condition of equilibrium is achieved somewhat later, since the true expression of the rate is $K_1 \varphi C$, and not $K_2 C$. Nevertheless, we can assume that the oxidation from both sides of sodium-butadiene rubber of thickness not greater than 1.0 cm. takes place practically under the conditions of fixed distribution of oxygen.

This assumption enables us to investigate the curvilinear relation of the rate of oxidation to the concentration of oxygen; this relation amounts to a solution of the equation:

$$D \frac{\partial^2 C}{\partial x^2} = K_1 \sqrt{C} \quad (6)$$

The solution of this equation:

$$x = \frac{1}{2} \sqrt{\frac{3D}{K_1}} \int_{C_0}^C \frac{dC}{\sqrt{C^3 - C_1^3}} \quad (7)$$

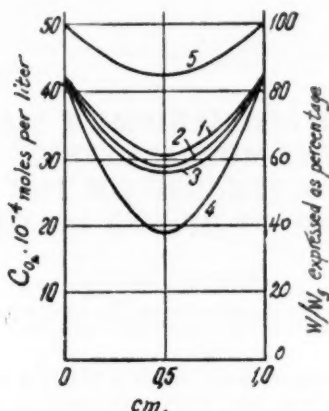


Fig. 3.—Distribution of oxygen concentrations and rates of inhibited oxidation of rubber. Temperature 120° C. 1. Fixed distribution calculated according to formula $W = K\sqrt{C}$. 2. The same, calculated according to the equation: $W = K\sqrt{C}$. 3. Distribution of oxygen 25,000 seconds from the beginning of the experiment. 4. The same 10,000 seconds from the beginning of the experiment. 5. Distribution of relative rates of oxidation at fixed distribution given in Curve 1.

where C_1 is the concentration of oxygen in the middle of the sheet and C_0 the concentration on the surface, is the solubility of oxygen in rubber.

The solution of the elliptic integral (7) has the form:

$$x = \sqrt{\frac{3D}{K_1}} \sqrt[3]{C_1} \left\{ \frac{1 + \sqrt{3}}{\sqrt{3}} F(\chi, \varphi) - 2\sqrt{3}E(\chi, \varphi) + 2\sqrt{3} \tan \frac{\varphi}{2} \sqrt{1 - \chi^2 \sin^2 \varphi} \right\} \quad (8)$$

where F and E are the normal Legendre forms of the elliptic integrals of the first and second type, K is the Legendre parameter ($\chi = \sin 15^\circ$), $\varphi = 2 \arctan \left[\frac{\sqrt{C/C_1 - 1}}{\sqrt{3}} \right]$.

In Figure 3, curve 1 shows the fixed distribution of oxygen concentration in a sheet 1 cm. thick, calculated according to Equation (8). Curve 5 shows the corresponding distribution of rates of uninhibited oxidation at different depths.

Apparently the rate of oxidation in the middle of a layer of rubber is about 85 per cent of that on the surface, i.e., inhibited oxidation of even such a comparatively thick sheet is almost uniform throughout the layer.

This applies to the static oxidation of rubber in the presence of an inhibitor. The picture changes sharply in the case of an activated process, and particularly if the raw rubber itself or vulcanized rubber is subjected to repeated deformation, i.e., if the process is activated mechanically. Likewise, rubber products in service and rubber being plasticized and processed in the course of manufacturing operations undergo such mechanical activation.

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- ² A good antioxidant type of inhibitor is a substance which, in very small percentages, inhibits the formation of side chains.
- ³ Rubber mixtures used in industry almost always contain antioxidants. See Kuzminskii, Meizels, and Leshnev, *Repts. Acad. Sci.* **71**, 2 (1950).
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STUDIES OF THE MECHANISM OF MASTICATION OF RUBBER. III. THE MUTUAL EFFECTS OF ORGANIC BASES AND SOFTENERS ON THE VISCOSITY LOWERING OF RUBBER SOLUTIONS *

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In Part II of this study, it was conceived that the viscosity-lowering of a rubber solution by softeners, such as benzoyl peroxide or thiols, depends on radical decomposition.

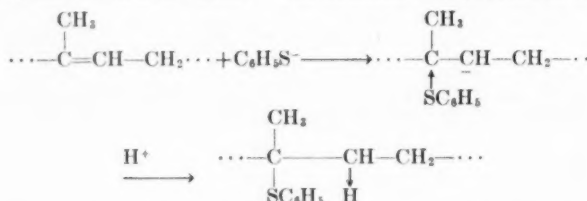
For instance, thiophenol decomposes as follows:



But coexisting with an amine, this softener may decompose into ions as follows:



If the ionic decomposition occurs, the softener adds to a double bond of rubber hydrocarbon and does not break down the hydrocarbon molecule, as reported by Kharasch and Fuchs¹. The addition may proceed as follows:



In this paper, the simultaneous action of amine and softener on rubber solutions was investigated.

WITH FURFURANTHIOL AND FURFURYLAMINE

Five cc. of a benzene solution of smoked-sheet rubber and 1 cc. of a benzene solution of furfuranthiol were introduced into an Ostwald viscometer. The concentrations of rubber and thiol in the mixture were 1 and 0.01 per cent, respectively.

First, the changes of viscosity with time were observed at 40° and 50° ± 0.1° C. The results are shown as the curves 1 and 2 in Figure 1.

In the figure, η_{rel} is (dropping time after certain time)/(dropping time at the start).

* Reprinted from the *Journal of the Institute of Polytechnics, Osaka City University, Japan*, Vol. 1, No. 2, pages 73-79, October 1950. Part I, on the "Viscosity Lowering of Rubber Solutions by Some Organic Bases", was published in this same issue, pages 59-64; Part I₂, on the "Viscosity Lowering of Rubber Solutions by Softeners", in the same issue, pages 65-72.

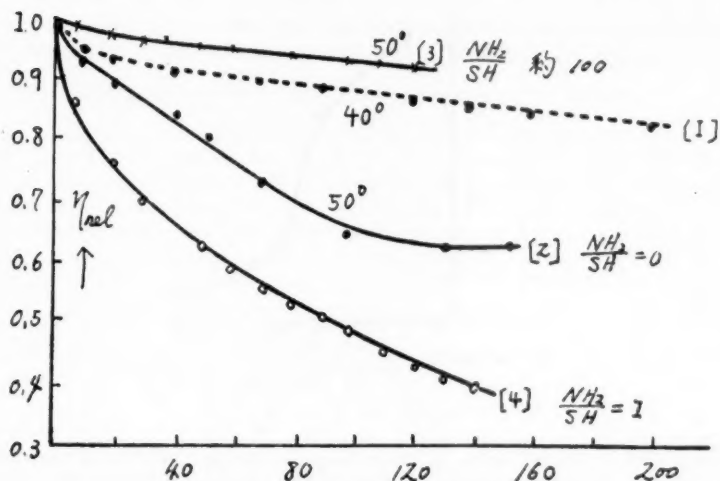


FIG. 1.

Next, 0.5 cc. or 0.0007 gram of furfurylamine was added, respectively, to 6 cc. of the mixture mentioned above, and the changes of viscosity were observed at $50^\circ \pm 0.1^\circ \text{C}$. The results are shown in Figure 1, as curves 3 and 4. In the figure (NH_2/SH) are the molar ratios of furfurylamine to furfuranthiol.

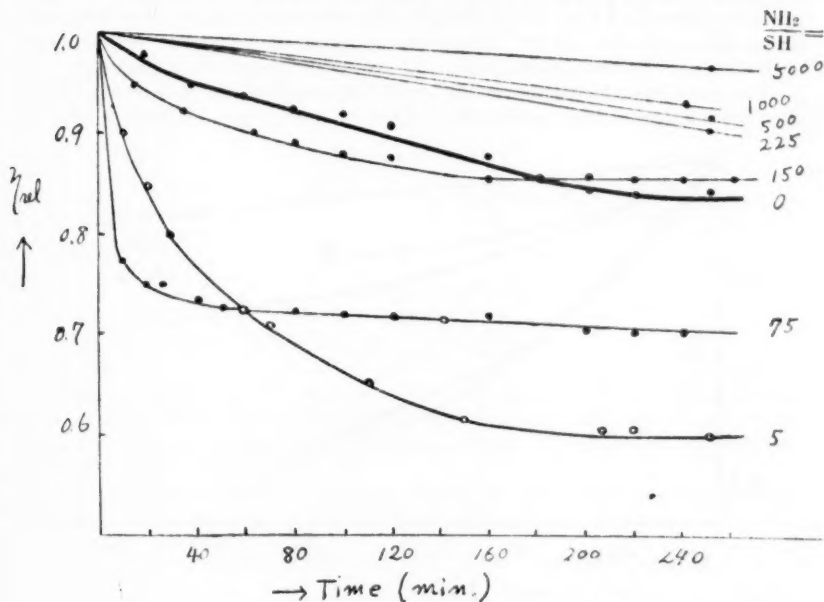


FIG. 2.

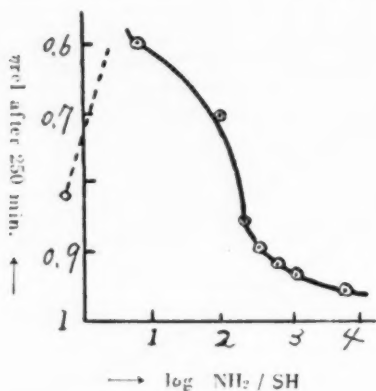


FIG. 3.

As indicated by these curves, in the presence of a large quantity of the amine, the viscosity lowering was smaller than in the absence of the amine. If the quantity of amine was small, the viscosity of the rubber solution was decreased greatly by the softener.

WITH THIOPHENOL AND FURFURYLAMINE

Smoked sheet and thiophenol were separately dissolved in benzene. Their concentrations were 0.28 and 0.0056 per cent, respectively. Five cc. of the rubber solution and 1 cc. of the thiophenol solution were mixed in an Ostwald viscometer with 1 cc. of the furfurylamine benzene solution at various concentrations. The results obtained at $50^\circ \pm 0.1^\circ \text{C}$ are shown in Figure 2.

The same deduction as in the case with furfuranthiol can be derived. Further, for the sake of easy appreciation, Figure 3 was drawn. This is a coordi-

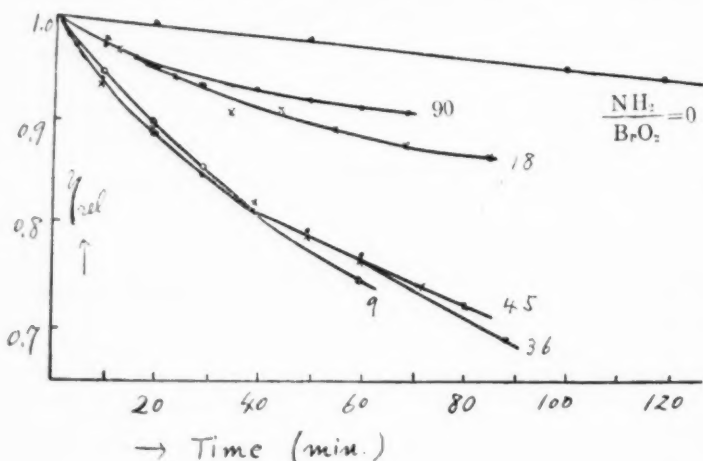


FIG. 4.

nate of the molar ratio of NH_2/SH and η_{rel} after 250 minutes. It is clear that the viscosity lowering is maximum when the ratio of NH_2/SH is 3-10.

WITH BENZOYL PEROXIDE AND FURFURYLAMINE

A 0.966 per cent solution of the deproteinized rubber in toluene was prepared, and 2 cc. of this rubber solution, 2 cc. of benzoyl peroxide solution in toluene (concentration $0.05 \cdot 10^{-5}$ mol.) and 1 cc. of furfurylamine-toluene solution of various concentrations were pipetted in an Ostwald viscometer. The molar ratio of rubber as C_5H_8 to benzoyl peroxide was 44:1. Viscosity measurements were carried out at $50^\circ \pm 0.1^\circ \text{C}$.

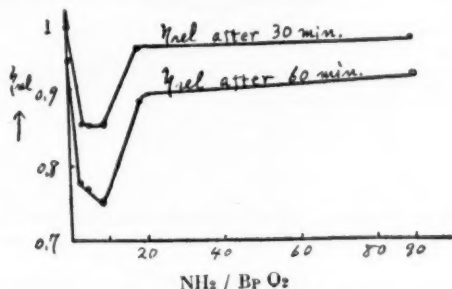


Fig. 5.

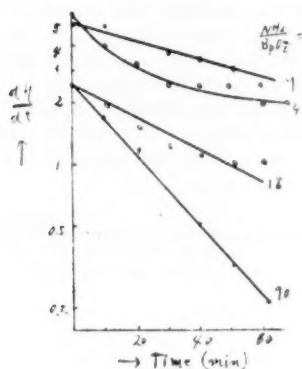


Fig. 6.

Figure 4 shows the changes of viscosity with time. NH_2/BPO_2 denotes the molar ratio of furfurylamine to benzoyl peroxide. η_{rel} after 30 minutes or 60 minutes is shown in Figure 5. When the ratio of NH_2/BPO_2 is 5-10, the decrease of viscosity is maximum.

The velocity of viscosity-lowering $d(\eta_{\text{rel}})/dt$ was calculated as shown in Figure 6. It is not clear why the decrease of $d\eta/dt$ is so large.

WITH β -NAPHTHALENETHIOL AND FURFURYLAMINE

0.0502 gram of RPA-2 (a softener from the du Pont Co., which is a mixture of β -naphthalenethiol in $\frac{1}{3}$ part and solid paraffin in $\frac{2}{3}$ parts) was dissolved in

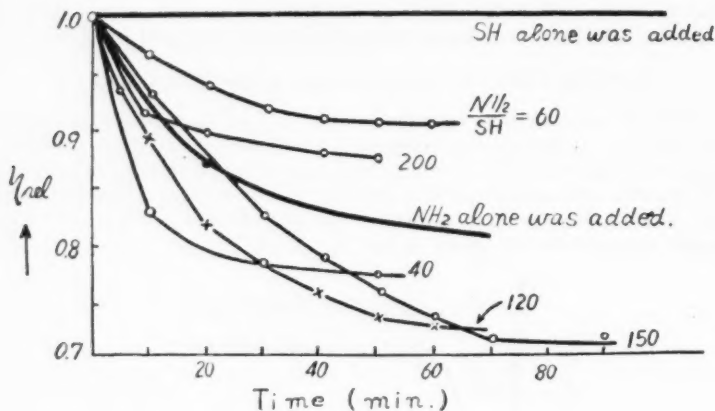


FIG. 7.

toluene and made up to 10 cc. Smoked sheet was dissolved in toluene to make a 1.937 per cent solution. 1.4300 grams of furfurylamine was dissolved in 25 cc. of toluene.

First, 1 cc. of the rubber solution and 0.4–3 cc. of the RPA-2 solution were mixed and made up to 5 cc. with toluene. The mixture was introduced in an Ostwald viscometer, and the viscosity was measured at $50^\circ \pm 0.1^\circ \text{C}$. But after 120 minutes there was almost no change of viscosity.

Second, 1 cc. of the rubber solution, 1 cc. of the amine solution, and 3 cc. of toluene were mixed, and the changes of viscosity with time were measured. The results obtained are shown in a curve denoted by NH_2 in Figure 7.

Third, 1 cc. of the rubber solution, 1 cc. of the amine solution, and 0.3–1.5 cc. of the RPA-2 solution were mixed and made up to 5 cc. with toluene. The

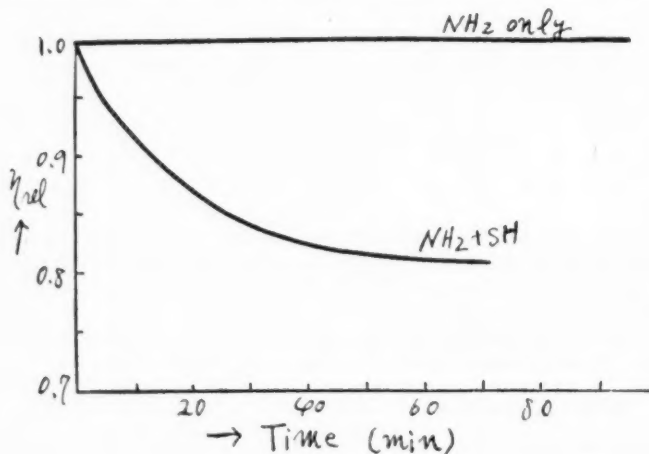


FIG. 8.

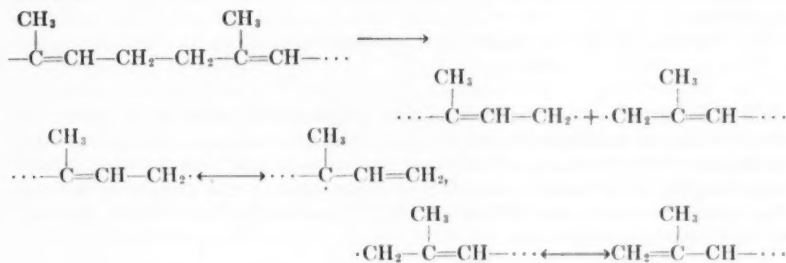
changes of viscosity of the mixtures were observed at $50 \pm 0.1^\circ \text{C}$. The results obtained are in Figure 7. Thus it becomes clear that β -naphthalenethiol in such a small quantity as used here could decrease the viscosity of the rubber solution only in the presence of amine.

And fourth, *vice versa*, furfurylamine in a smaller quantity could decrease viscosity of the rubber solution in the presence of β -naphthalenethiol. It is shown in Figure 8. This experiment was carried out in two runs, using 1 cc. of the rubber solution, 0.4 cc. of the RPA solution, and 0.1 cc. of the amine solution.

DISCUSSION

As stated above, it is clear that an amine in the quantity of 1 to 10 times of a softener can increase the viscosity lowering of the rubber solution by softener but an amine in large quantity decreases *contrarywise* the action of the softener. These phenomena can be explained by the following assumption. As reported in the previous paper and in this paper, the viscosity of natural rubber and deproteinized rubber likewise went down. So it was proved that the change of viscosity was caused by scission of the rubber hydrocarbon molecule.

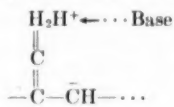
Scission of the hydrocarbon molecule occurs at the link of $-\text{CH}_2-\text{CH}_2-$ *i.e.*, β -position to the double bond. And it is conceivable that the reaction is a radical decomposition which is facilitated by generation of the allyl radicals as follows:



For this electronic displacement, π -electrons of the double bond must move. The effect of hyperconjugation of the CH_3 groups answers this purpose, as follows:



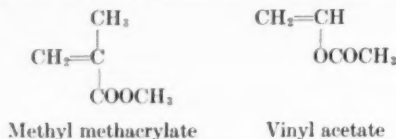
When a base is present, the effect of hyperconjugation may increase, because the base can attack the proton from the methyl groups.



So the presence of a base makes easy the scission of the chain of rubber hydrocarbon.

But if the quantity of the amine is large, $R-SH$ decomposes completely into ions. Accordingly the change of viscosity becomes small.

Lately, Noma, Nagai, and Nishimura² reported that dimethylaniline can promote the polymerization of methyl methacrylate catalyzed by benzoyl peroxide, but does not exert any action on the polymerization of vinyl acetate.



As their formulas show, only in the molecule of methacrylate is there a typical form of hyperconjugation of $\text{CH}_3-\text{C}=\text{C}-$. So the results obtained by Noma, Nagai, and Nishimura² can be explained by the theory stated above.

SUMMARY

1. A large decrease in viscosity of a rubber solution was observed with the addition of furfurylamine in a quantity ten times as much as the softener used, such as furfuranthiol, thiophenol, β -naphthalenethiol, or benzoyl peroxide, but a small change with the addition of a large quantity of an amine, until finally reaching to a point where the decrease was less than that when only a softener was added.

2. For this reason, the following hypothesis is presented. Hyperconjugation



of the group $\cdots\text{C}=\text{CH}\cdots$ in the hydrocarbon molecule of rubber increases with the addition of a small amount of an amine, promoting the rearrangement of the electron pairs of the double linkage, but with the addition of a large quantity of the amine, dissociation of the softener into its ionic form takes place and, as a result, the softener merely adds on to the double bond, the rubber molecule being unbroken.

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INVESTIGATIONS OF THE REVERSION OF VULCANIZED RUBBER UNDER HEAT *

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When rubber mixes are vulcanized by heating, there is a progressive increase in the modulus (*i.e.*, the stress at a given elongation) of the vulcanizate and a decrease in elongation at a given stress. On continued heating the modulus may begin to decline after reaching a maximum, and the elongation at a given stress may increase after attaining a minimum value. This setback in vulcanization, called reversion, was originally observed by de Vries and Hellen-doorn¹ in rubber mixes containing up to 6 per cent of sulfur. Schidrowitz and Goldsbrough² found that reverted samples contained very little uncombined sulfur and suggested that reversion was caused by heat degradation of rubber after the integrating action of free sulfur had stopped. Vulcanization is now believed to consist of the introduction of sulfur cross-linkages among linear rubber molecules and conversion of them into a 3-dimensional network³, and various theories have been put forward to explain reversion on the basis of cross-linkage breakdown. Garvey⁴ proposed a physical mechanism based on *cis-trans* isomerization. Studies on the dispersibility of rubber-sulfur and rubber-sulfur-zinc oxide stocks in solvents containing piperidine led Farmer⁵ to conclude that reversion was caused by a change in the chemical nature of cross-linkages and not by their destruction. Dogadkin and coworkers⁶ attempted a mathematical explanation of the maximum tensile strength attained by a rubber mixture during vulcanization. Stiehler and Wakelin⁷, and Williams⁸ considered reversion to be a physical phenomenon. According to recent theories⁹ the modulus of vulcanized rubber at a given temperature is a function of the concentration of cross-linked units, and it is enhanced if stretching causes chains to crystallize. Reversion may arise either by a decrease in the concentration of the cross-linked chains and (or) structural modification of cross-linked chains affecting their crystallization. There is, however, no chemical evidence to support these views.

Sulfur reacts with simple mono- and polyolefins (including polyisoprenes)¹⁰ to yield polysulfide as primary products. The only evidence for the presence of polysulfides in vulcanized rubber is the observation¹¹ that sodium sulfite solution extracts about 3 per cent of combined sulfur from samples from which all free sulfur has been extracted. Recent work¹² has shown that sulfur linkages produced during vulcanization may be altered during the hot extraction of the vulcanizate adopted in the conventional methods of chemical analysis. The recognition of the radical mechanism of vulcanization and of the influence of traces of oxygen on the vulcanization reaction has led to attempts to study vulcanization in the absence of oxygen¹¹ and to carry out mastication and compounding in an atmosphere of nitrogen¹³. However, no study of vulcanization

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or reversion appears to have been made with adequate precautions against possible interference by secondary reactions from the stage of making the mixture to the stage of final chemical analysis. The chemical aspect of reversion under heat was, therefore, examined afresh and the results of the investigation are recorded in this paper.

METHODS

Vulcanization.—Sulfur was dissolved in ammonium polysulfide to give a total sulfur concentration of 11.2 per cent in solution. Requisite amounts of the solution were mixed with Dunlop's centrifuged latex (DRC, 64 per cent). An aqueous solution of hexamethylenetetramine was stirred in, if required. The mix, freed of air bubbles, was poured on level glass plates and allowed to dry at room temperature in darkness. The thickness of the sheets varied from 0.05 to 0.07 inch. Rectangular pieces, 5.5×1.25 inches, were cut out from the sheet; the variation in thickness of individual samples was <0.002 inch. The

TABLE I
COMPOSITION OF MIXES AND CONDITIONS OF CURE

No. of cure	Composition of mix (parts by wt.)	Atmosphere of cure	Temperature of cure (° C)
1	{ Rubber 100 Sulfur 4.8 }	Nitrogen	162
2	{ Rubber 100 Sulfur 4.8 }	Air	162
3	{ Rubber 100 Sulfur 5.7 }	Nitrogen	152
4	{ Rubber 100 Sulfur 5.7 }	Air	152
5	{ Rubber 100 Sulfur 3.5 Hexamethylene- tetramine 1.25 }	Nitrogen	141
6	{ Rubber 100 Sulfur 3.5 Hexamethylene- tetramine 1.25 }	Air	141

samples were analyzed for their sulfur content. Vulcanization of the samples was carried out in nitrogen and in air. For nitrogen cures, samples were kept for 10 days under vacuum (0.05 mm. pressure), saturated with pure nitrogen, then vulcanized in an atmosphere of nitrogen. The escaping gas was tested for hydrogen sulfide. For air cures, samples were wrapped in aluminum foil and vulcanized in an air oven.

Testing.—The tensile data were obtained on a Scott machine. The specific gravities of the samples were determined and experiments on equilibrium swelling were carried out in the usual way¹⁴ at room temperature and in darkness. The amount of benzene taken up by the samples was determined by weighing them in stoppered weighing bottles. Free sulfur was determined by extraction with cold isopentane (in some cases with hot isopentane, and cold and hot acetone), drying the extract under vacuum, extracting sulfur with aqueous sodium sulfite, and titrating the resulting thiosulfate with iodine¹⁵. The KClO_3 - HNO_3 method¹⁶ was used for estimating free sulfur in the earlier ex-

TABLE II
TENSILE DATA OF SAMPLES CURED UNDER DIFFERENT CONDITIONS

Cure no.*	Heating period (hr.)	Modulus at 500% elongation (lb. per sq. in.)	Tensile strength (lb. per sq. in.)	Elongation at break (%)
1(162)	1.5	160	1,54	1,050
	3	130	1,320	1,075
	4.5	110	900	1,100
2(162)	1	159	1,760	1,025
	1.5	120	1,330	1,025
	3	80	820	1,100
3(152)	4.5	60	720	1,125
	2	213	3,240	875
	3	239	2,900	900
4(152)	4	236	2,120	900
	5	226	2,060	900
	1	170	1,660	850
5(141)	2	300	1,890	900
	3	250	1,890	850
	4	219	1,600	875
6(141)	5	200	1,600	925
	2	120	2,430	1,100
	3	120	2,400	1,100
7(141)	4	161	2,600	1,125
	1	153	2,380	1,000
	2	112	1,240	1,100
8(141)	3	77	1,100	1,100
	4	120	1,580	1,075

* Temperature ($^{\circ}$ C) of cure given in brackets.

periments. Combined sulfur was determined by the bromine-nitric acid method¹⁷. The methyl iodide reactions were based on the method used by Selker and Kemp¹⁸.

The composition of the mixes employed and the curing conditions are given in Table I.

RESULTS

The results of the tensile tests with different samples are recorded in Table II.

The tensile data (Table II) show that (1) reversion occurred in all cures except in cure 5; (2) in cure 6 reversion was of a brief duration, after which the modulus again rose¹⁹; (3) reversion in nitrogen occurred at a slower rate than in

TABLE III
EXTRACTION OF SULFUR FROM SAMPLES CURED IN NITROGEN AND IN AIR

Solvent	Temperature of extraction ($^{\circ}$ C)	Period of extraction	Nitrogen cure		Air cure	
			Extract, % on vulcanizate	Free S, % on vulcanizate	Extract, % on vulcanizate	Free S, % on vulcanizate
Cold isopentane	25	10 days	0.60	0.25	2.7	0.51
Cold acetone	25	14 days	—	—	2.4	0.39
Cold acetone after 10 days in cold isopentane	25	3 days	2.80	0.00	2.4	0.00
Hot isopentane	29	14 hr.	0.83	0.42	3.4	0.70
Hot acetone	57	8 hr.	—	0.20	4.1	0.47

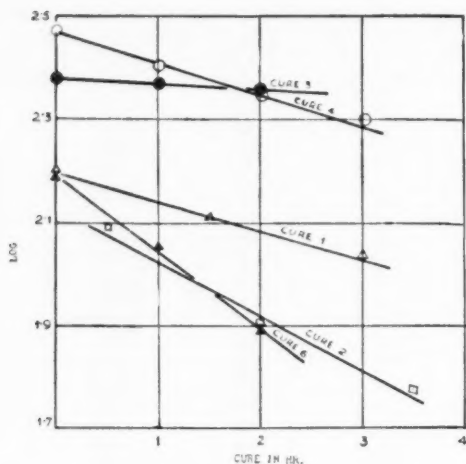


Fig. 1.—Relationship between reverting modulus of vulcanizate samples and time of cure.

TABLE IV
FREE AND COMBINED SULFUR DURING REVERSION

Cure no.*	Time of heating (hr.)	Free S (% on vulcanizate)		Combined S (% on extracted residue)	C/H ratio
		0.51†	0.22‡		
1(162)	1.5†	0.51†	0.22‡	4.90	—
	3.0	0.39	0.08	4.30	—
	4.5	0.45	0.22	3.80	—
2(162)	1.0	0.41	—	4.30	—
	1.5	0.39	—	4.50	—
	3.0	0.51	—	4.80	—
3(152)	4.5	0.56	—	4.30	—
	3.0	0.42§	0.25	5.83	7.66
	4.0	0.44	0.30	5.61	7.61
4(152)	5.0	0.41	0.20	5.61	7.68 (cf. 7.44 for C ₅ H ₈)
	3.0	0.70	0.51	5.60	—
	4.0	0.16	0.10	6.09	—
5(141)	5.0	0.21	0.03	5.71	—
	2.0	1.00	0.98	2.76	—
	3.0	0.69	0.66	3.17	—
6(141)	4.0	0.33	0.40	3.14	—
	1.0	1.60	1.60	2.15	—
	3.0	1.00	0.81	2.94	—
	4.0	0.67	0.51	3.00	—

* Temperature (° C) of cure given within brackets.

† Oxidation by KClO₃-HNO₃ mixture.

‡ Extraction by cold isopentane. In cures 3 and 4 the residues were left for over a week before estimating S.

§ Extraction by hot isopentane.

air. It was observed that the reverting modulus falls exponentially with time (Figure 1).

Free and combined sulfur in samples during reversion.—Several experiments were carried out to determine the most efficient method of extracting samples. The results of trials with different solvents are recorded in Table III. It was observed that (1) isopentane extracts more sulfur than does acetone; (2) hot extraction is more efficient than cold extraction; (3) 7 to 10 days' immersion of samples in cold isopentane extracts all free sulfur.

The amounts of free and combined sulfur in various samples which suffered reversion are given in Table IV.

The following conclusions may be drawn from the results presented in Table IV: (1) the free sulfur present in the vulcanizate, when reversion sets in, is far from insignificant, as hitherto supposed; (2) the increase in the free sulfur content and the decrease in combined sulfur content of the samples during a given cure indicate the presence of polysulfides. Free sulfur has been previously reported to increase during heat aging²⁰.

NUMBER OF CROSS-LINKAGES IN THE CURED SAMPLES AND REVERSION

Cross-linkages.—Data on the swelling characteristics of samples in benzene have been used in deriving the factors employed in calculating the number of

TABLE V

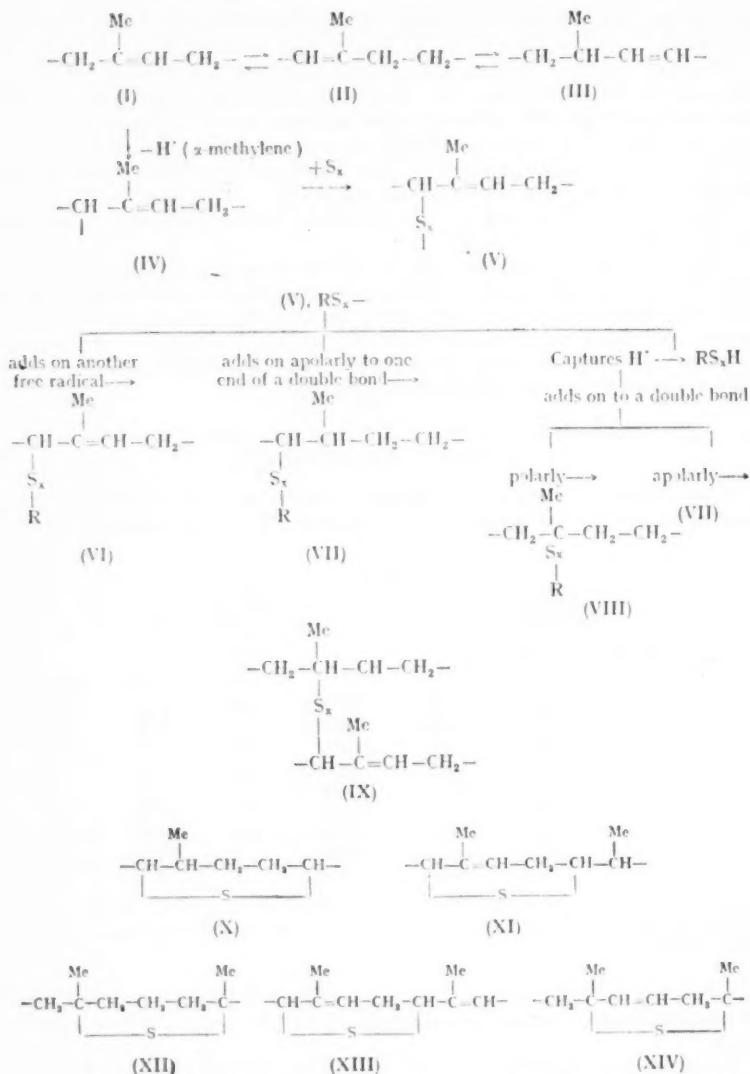
Cure no.	Heating period (hr.)	Benzene absorbed per cc. of sample (cc.) (Q)	$1/Q+1$ (r_2)	V_c	Moles of cross-links per 100 gram sample ($\frac{1}{2}M_c$) $\times 100$	$\rho \times 100$	$M_c \times 10^{-2}$
3	3	4.41	0.185	9,100	0.58	0.78	8.7
	4	4.43	0.184	9,100	0.58	0.78	8.7
	5	4.60	0.178	10,000	0.52	0.71	9.6
4	3	4.40	0.185	9,100	0.58	0.78	8.7
	4	4.59	0.179	9,500	0.55	0.75	9.1
	5	4.80	0.172	10,300	0.51	0.69	9.9
6	1	5.95	0.144	15,800	0.34	0.46	14.9
	3	6.30	0.137	17,000	0.32	0.43	16.0
	4	5.90	0.145	15,600	0.34	0.46	14.7

$V_c = V_1 r_2^2 \ln(1 - r_2) + r_2 + \mu r_2^2$, where V_1 is the molar volume of solvent = 89.0; μ = interaction energy parameter = 0.40.

M_c = mol. wt. between cross-links = $V_c \rho d$, where d = sp. gr. ρ = fraction of isoprene units cross-linked = $68/M_c$.

cross-linkages in cured samples (Table V). Chemical methods are not available for determining the number of cross-linkages and so to confirm the calculated values.

Flory and coworkers²¹ varied the value of $\rho \times 100$ from 0.1 to 4.0 in rubber mixes vulcanized by azodicarboxylates, but the modulus was not found to fall after a certain maximum limit. According to Goppel²², crystallization plays a negligible role in modulus changes at low elongations. According to the results obtained here, the temperature of cure is a vital factor in governing reversion. At 152° C, the value of $\rho \times 100$ drops by 11.5 per cent in cure 4, and by 9 per cent in cure 3, while at 141° C the drop is 6.5 per cent in cure 6. This shows that reversion is caused by a breakdown of cross-linkages in the vulcanizate molecule and (or) scission of chains.



The linear relationship discovered between the log of the reverting modulus and the time of heating can be derived thus:

If ν is the number of cross-linked chain sections supporting the stress per unit volume, the rate of breakdown is given by:

$$-d\nu/dt = K\nu$$

$$-\int d\nu/\nu = k \int dt$$

or

$$-\ln v = kt$$

where K is the velocity constant.

According to the statistical theory of rubber elasticity:

$$v \propto M$$

$$\therefore -\ln M = kt$$

or

$$-2.3 \log M = kt$$

M being the modulus.

Thus $\log M$ is directly proportional to the time of cure, and the slope of the line is the reaction rate constant k . Figs. 2-4 show the plots of $\log M$ against t

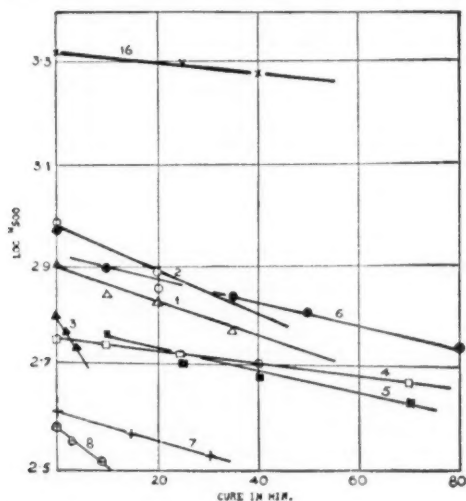


FIG. 2.—Relationship between reverting modulus of vulcanizate samples and time of cure.

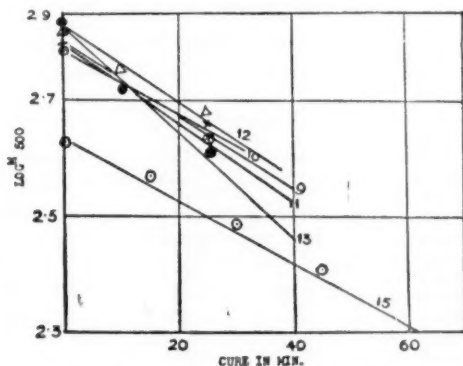


FIG. 3.—Relationship between reverting modulus of vulcanizate samples and time of cure.

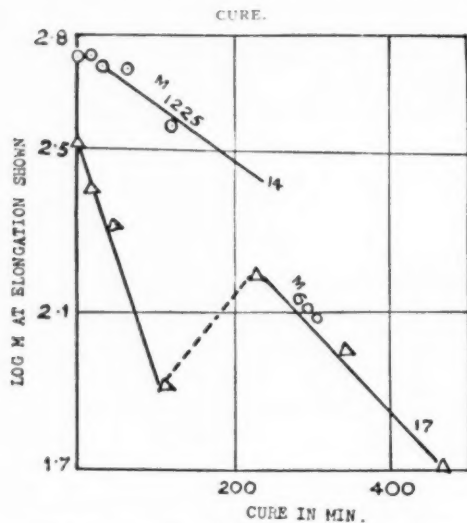


Fig. 4.—Relationship between reverting modulus of vulcanizate samples and time of cure.

for 17 instances of reversion taken from literature²³.

From k the molar free energy of activation, ΔF , can be calculated thus:

$$k = (RT/Nh) \cdot e^{-\Delta F/RT}$$

where R , gas constant; T , absolute temperature; N , Avogadro's number; h , Planck's constant.

The calculated values of ΔF are tabulated in Table VI.

The value of ΔF may be taken as 33.3 ± 1.7 kcal., irrespective of the atmosphere or the temperature of cure or the composition of mixture. The values of ΔF for breaking one —S—S— link and a peroxide link are 27.5 and

TABLE VI
MOLAR FREE ENERGY OF ACTIVATION

Reference to data	Temperature of cure (° C)	ΔF /mole (kcal.)
Cure 1	162	34.8
Cure 3	152	35.1
Cure 4	152	33.8
Cure 6	141	32.1
Figs. 2-4		
Graph No. 1	142	32.0
Graph No. 2	142	32.0
Graph No. 3	153	31.8
Graph No. 4	142	32.9
Graph No. 5	142	32.4
Graph No. 6	142	32.4
Graph No. 7	142	32.4
Graph No. 8	153	32.2
Graph No. 15	132	31.6
Graph No. 16	142	32.9

34 kcal., respectively²⁴. The ΔF for reversion is thus sufficient to rupture polysulfide linkages. The use of an antioxidant or exclusion of oxygen does not prevent the occurrence of reversion in a sample if the temperature is high enough to provide the required ΔF .

Additional proof for the presence and breakdown of polysulfide is provided by the methyl iodide reaction of reverted samples, at room temperature, in the absence of oxygen and light. It is known that: (1) sulfur can be removed in 1-2 days as trimethylsulfonium iodide (Me_3SI) from dialkenyl polysulfides and monosulfides, or alkenylalkyl (tertiary carbon) monosulfides, in inter- or intramolecular linkages. Alkyl polysulfides react more slowly; (2) liberation of iodine in 1-2 days is an indication of the presence of dialkyl, alkylalkenyl, or dialkenyl di- and polysulfides. The ratio of the moles of iodine liberated to the moles of methyl iodide reacted indicates the type of linkage; (3) sulfur can be removed in 1-2 days, without releasing Me_3SI , from alkylalkenyl monosulfides, disulfides, and polysulfides. The alkyl link is severed on prolonged reaction, with deposition of Me_3SI . (The alkenyl link means here the α -methylenic type of unsaturation.)

The methyl iodide reaction of cured samples shows that (1) as reversion progresses, the rate of methyl iodide reaction increases for a given cure. The ratio of gram-atoms of combined sulfur removed to moles of MeI reacted is >0.5 in the beginning of reversion in cures 3 and 4; this may be due to polysulfides. In cure 6, the accelerator has apparently caused a decrease in the number of sulfur atoms in the cross-linkages—a rapid reaction rate indicates a preponderance of mono- and disulfides with α -methylenic linkages; (2) iodine is liberated in 24 hours in all cases; (3) Me_3SI is formed in 5-6 days in air-cured samples, but almost none is produced in nitrogen-cured samples, even after 30 days. This indicates the absence of diallylic or allyl-tertiary-C-alkyl linkages in nitrogen cures.

On the basis of the above data the following mechanisms are proposed for vulcanization and reversion of rubber in nitrogen and in air.

On heating types VI, VII, VIII, the value of x (originally, say, 6) decreases to 2 or 1. In nitrogen cures the formation of type VI is ruled out, as it gives Me_3SI ; the formation of types VII or IX from III are indicated.

For air cures, the formation of types VI and VIII are indicated.

Simultaneously with the occurrence of the intermolecular reactions outlined above, intramolecular reactions may also proceed, involving the radical RS_2 — and the thiol RSH . The value of x may be 1. In nitrogen cures, by analogy with VII, the formation of types X and XI are indicated.

In air cures the types indicated are: XII (cf. VIII), XIII (cf. VI), or XIV from III.

SUMMARY

(1) During reversion of a vulcanizate, the breakdown of cross-linkages, including those of polysulfides, predominates over any simultaneous reformation of cross-linkages.

(2) The reverting modulus falls exponentially with time.

(3) The calculated molar free energy of activation is 33.3 ± 1.7 kcal., irrespective of the temperature or the atmosphere of cure, or the composition of the mix, and is sufficient to rupture an $-\text{S}-\text{S}-$ bond.

(4) The degree of cross-linking, estimated from the equilibrium swelling measurements in benzene, falls during reversion.

(5) The exclusion of oxygen during curing does not prevent reversion if the temperature is high enough to supply the energy needed to break up the cross-linkages.

(6) During reversion in nitrogen, hydrogen sulfide is freely evolved, and the C/H ratio rises above the value for C_5H_8 .

(7) Evidence for the formation and breakdown of polysulfides during reversion is provided by an increase in free sulfur and a decrease in combined sulfur during a given cure, and the methyl iodide reaction of the reverted vulcanizates.

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AN INFRARED SPECTROMETRIC STUDY OF THE OXIDATION OF NATURAL RUBBER *

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INTRODUCTION

The kinetics of the oxidation of natural rubber by atmospheric oxygen has been studied by various methods, for example, by volumetric and manometric measurements of the absorption of oxygen, by measurements of the increase of weight of the rubber, and by changes in the mechanical properties as a function of time. However, the oxidation of rubber is a complex phenomenon, and none of these techniques offers a means of following the oxidation in detail.

In principle, it is possible, by infrared absorption spectrometry, to detect the presence of different groups which are present in a given sample of rubber and to determine their concentrations. Hence, it was hoped that this technique would offer a means of studying the various phenomena involved in the oxidation of rubber. In fact, this technique has already been employed in studies of the structure of rubber¹ as well as in the qualitative and quantitative analysis of synthetic products². In addition to these already published studies, various authors have reported that the oxidation of natural rubber results in changes in its infrared spectrum³, but none of the investigators has followed these changes quantitatively. Nevertheless, the possible interest of such a quantitative study, when carried out in parallel with a study of the changes in mechanical properties, has been pointed out by different authors⁴.

The authors of the present work decided, as a first approach to the problem, to prepare samples of rubber which could be studied by infrared absorption. The progress of oxidation could then be followed quantitatively by the disappearance of the principal groups present in rubber which had not undergone oxidation and the formation of characteristic groups in the oxidation products. Finally, from the data obtained, it was hoped, if not to draw conclusions as to the mechanism or mechanisms of oxidation, at least to obtain some indications of the precise kinetics of this oxidation.

EXPERIMENTAL RESULTS

PREPARATION OF THE SAMPLES

The experiments were carried out with pale crepe. The rubber was dissolved in petroleum ether, was recovered in the form of a film by evaporation of the solution in a vacuum, was treated with methanol and acetone to extract its natural antioxidants, was then dissolved in carbon tetrachloride, and the solution thus obtained was kept at 0° C in an atmosphere of pure nitrogen until ready for use.

The solution was used to prepare films on a smooth surface of rock salt. The films were oxidized on the rock salt surface in air in an oven maintained at

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Industrie Chimique Belge*, Vol. 16, No. 3, pages 133-137, 1951.

the desired temperature. The film of rubber on the rock salt substratum was withdrawn from time to time to take infrared spectra.

Vulcanized rubber also was studied. Ring test-specimens were tested for their mechanical properties and, at the same time, more of the same samples served for the spectroscopic measurements. In the preparation of the samples for the latter measurements, certain difficulties were encountered, for solution of the samples was impossible. No success was had in preparing films sufficiently thin by means of a microtome, and resort was finally had to grinding the samples at a low temperature. However, even after lowering the temperature of the samples to that of liquid nitrogen, grinding did not give a powder fine enough to be usable for taking spectra under ideal conditions. Another expedient was to treat the samples with carbon tetrachloride, to remove a certain quantity of the gel obtained, and to compress this between two plates of rock salt to the point where the thickness was correct for taking the infrared absorption spectrum.

TAKING OF THE INFRARED ABSORPTION SPECTRA AND THE CALCULATION FROM THE SPECTRA OF THE CHANGES OF CONCENTRATION OF THE DIFFERENT ATOMIC GROUPS DURING THE OXIDATION PROCESS

The extinction of the samples of rubber studied was measured as a function of the wave length, both before and after oxidation, by means of a Beckman infrared spectrometer of the I.R.2 type. From the total extinction for each wave length, corresponding values of the concentrations of the following groups were calculated: $C=O$, $C-O$, OH , $R-C(CH_3)=CHR$, $C=C$, CH_3 , and CH_2 . In these calculations, account was taken of the possible superposition of the absorption bands of the various groups, of the phenomena of reflection at

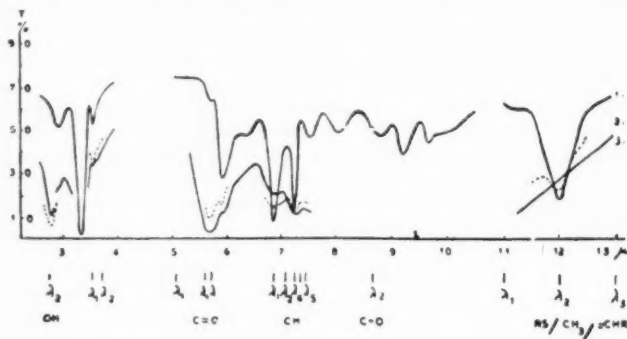


Fig. 1.—Evolution of the spectrum as a function of time: (1) t_1 ; (2) $t_2 > t_1$; (3) $t_3 > t_2$.

different interfaces, of diffusion by the sample, and of absorption by the substratum of rock salt⁵.

Figure 1 gives an idea of the development of the spectrum of a sample, maintained at a constant temperature, as a function of time, and it shows the wave lengths which were used as a means of calculating the concentrations.

Figure 2 shows the changes of concentration of different groups under the same conditions. These changes are shown as moduli in such a way as to make

easy a comparison between the behavior of the various groups. For convenience, the abscissa represents the logarithm of time. It is evident that the concentration of OH groups increases at first with continuing oxidation, as does

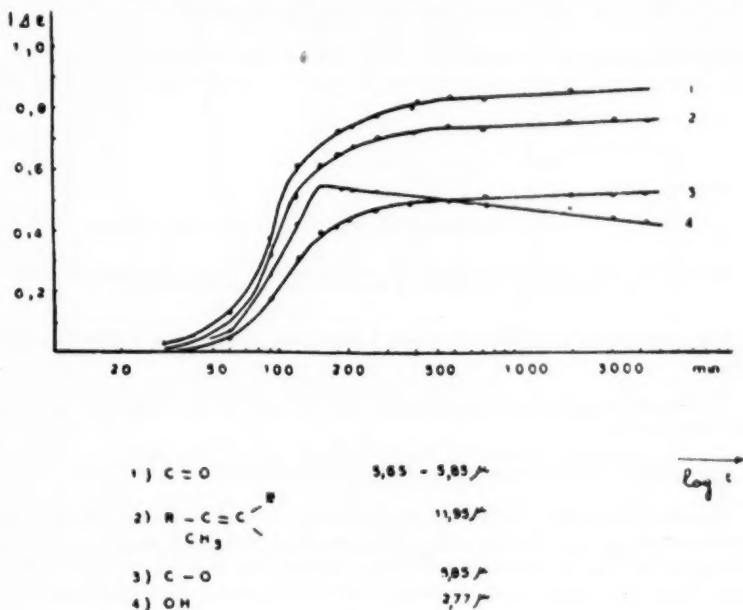


Fig. 2.

that of the other groups, then decreases after a rather short time. The moment is, therefore, soon reached when the process or the processes which lead to the disappearance of the OH groups exceed the process or processes which produce these groups.

SPECIAL STUDY OF THE $C=O$ GROUP

The fundamental band of the $C=O$ group is located at approximately 5.75μ , but it varies slightly according to whether the compound concerned is an aldehyde, a ketone, or an acid. Since each of these functions is probably a product of the oxidation of natural rubber, it should be expected that the absorption in the region of 5.75μ would be complex. As a matter of fact, at the beginning of oxidation, two bands can be distinguished, one at 5.85μ , the other at 5.65μ , which develop with unequal rapidity. With increase in absorption at these two wave lengths, these two bands become progressively more superimposed until the time comes when they practically blend into a single broad band.

This explains why, in the first part of this investigation, the authors were reconciled to following the total absorption due to the different $C=O$ groups by measurements of the extinction at the two different wave lengths. This explains also why Figures 1 and 2 show only the total concentration of $C=O$ groups.

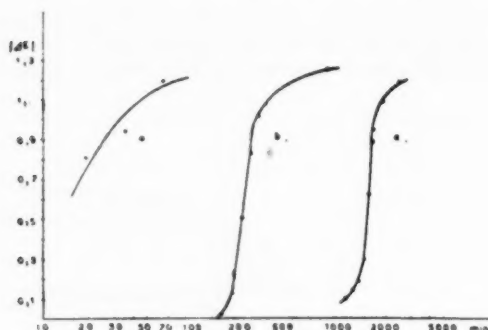


Fig. 3.—The C=O group during oxidation: (a) without antioxidant, but with benzoyl peroxide; (b) without either antioxidant or chain initiator; (c) with antioxidant.

The appearance of the C=O group was studied under three different conditions:

- (1) In pale crepe containing no antioxidant, but to which benzoyl peroxide had been added;
- (2) In pale crepe containing no antioxidant and no peroxide;
- (3) In pale crepe containing its natural antioxidant.

Figure 3 shows the changes in concentration of the C=O group under these three conditions. In the first case, oxidation took place at so rapid a rate from the beginning that it was not possible to construct the initial part of the curve. In the other two cases, on the contrary, there were long induction periods.

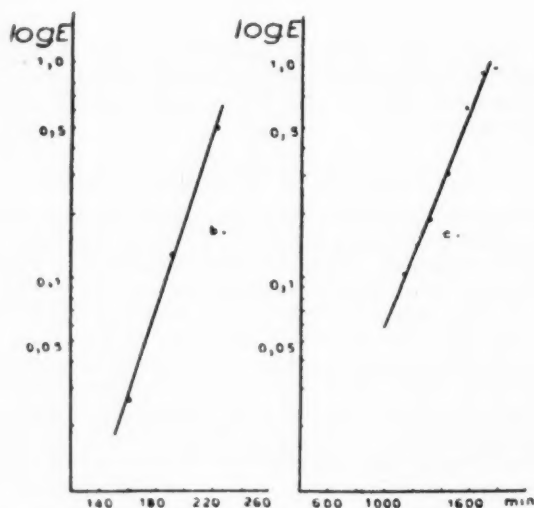


Fig. 4.—The C=O group in the course of oxidation: (b) without antioxidant; (c) with antioxidant.

If as ordinate, one plots, not the concentrations themselves but their logarithms, there is obtained, for the early stage of oxidation, a straight line representing the change as a function of the time, as may be seen in Figure 4.

INTERPRETATION OF THE RESULTS

The curves in Figure 5 show that, at the beginning of oxidation, the law of the change of concentration n of the C=O group as a function of time is an

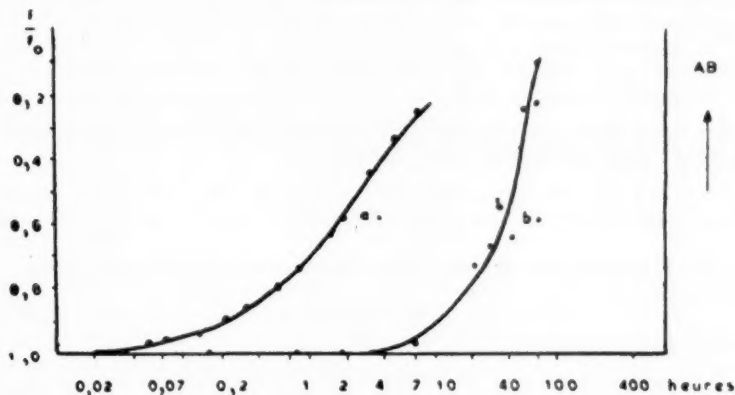


Fig. 5.—(a) Relaxation curve; (b) absorption curve of the C=O group.

exponential one:

$$n = Ce^{\phi t}$$

which corresponds to what is already known about chain reactions, not only of ordinary chains but also of degenerated chains which are characterized by the formation of a relatively stable product, decomposition of which can initiate a new primary chain.

It would seem, therefore, that the results observed can be explained by the following mechanism:

	Scheme
I. Chain initiation (formation of R- radical)	
$R \rightarrow R\cdot$	$A \rightarrow X$ (1)
II. Propagation of the primary chain	
$R\cdot + O_2 \rightarrow RO\cdot O\cdot$	$X + \dots \rightarrow Y$ (2)
$RO\cdot O\cdot \rightarrow R\cdot ROOH$	$Y + A \rightarrow M + X$ (3)
III. Branching of the primary chain	
$ROOH \rightarrow R'C=O + \dots$	$M \rightarrow N + \dots$ (4)
$ROOH \rightarrow R'C=O + R\cdot$	$M \rightarrow N + X$ (5)
IV. Rupture of the chain	
notably $R\cdot$ or $ROO\cdot$ + antioxidant	$Y \rightarrow \text{stable}$ (6)
stable product	$Y \rightarrow \text{products}$ (7)

Let the concentrations at time t be:

$$x \text{ for } X \quad m \text{ for } M \quad n \text{ for } N$$

and call k_1 , k_2 , and g of the specific rates of reactions (4), (5), and (6), respectively.

If now, we consider, beginning at the initiation of oxidation, a period sufficiently short for the concentration of A to be assumed as constant, the quantity of chain carriers X formed per unit time in unit volume at any given temperature can likewise be assumed to be constant. Let x_0 represent this last quantity. We shall then have:

$$\frac{dx}{dt} = x_0 + k_2 m - gx$$

and

$$\frac{dm}{dt} = kx - (k_1 + k_2)m$$

where k represents the proportionality coefficient between x and the number of primary chains (II) in unit time. Finally:

$$\frac{dn}{dt} = (k_1 + k_2)m$$

If it is assumed that at time $t = 0$, x and m are equal to 0, and writing:

$$\begin{aligned} a &= \frac{k_1 + k_2 + g}{2} \\ b &= g(k_1 + k_2) - kk_2 \\ c &= kx_0 \\ d &= \sqrt{a^2 - b} \end{aligned}$$

it is found that:

$$m_t = \frac{(a-d)c}{2bd} (e^{-(a+d)t} - 1) - \frac{(a+d)c}{2bd} (e^{(-a+d)t} - 1)$$

If b is less than 0, this relation becomes, for sufficient long t values, approximately equal to:

$$m_t = -\frac{a+d}{2bd} 2^{(-a+d)t}$$

and consequently:

$$n_t = -\frac{(2a-g)(a+d)c}{2bd(d-a)} e^{(-a+d)t}$$

where $n_t = Ce^{\phi t}$, as shown experimentally.

If an antioxidant is added, the rate of disappearance of the chain carriers increases, g increases, and b becomes smaller in modulus, and may annul itself, in fact may even become negative.

If, however, the concentration of antioxidant remains moderate, so that b remains negative, the law of formation of C=O groups remains exponential, but the coefficient ϕ becomes smaller and the time for $\log n$ to become zero, i.e., $\log C/\phi$, becomes greater. This is evident in Figure 5, which shows the experimental results. The angular coefficient of the curve: $\log n = f(t)$, becomes smaller and the induction period becomes longer.

COMPARISON OF THE RESULTS OBTAINED IN THE SPECTROSCOPIC STUDY WITH THE RESULTS OF MEASUREMENTS OF THE MECHANICAL PROPERTIES

From measurements, using a Tobolsky balance⁶, of a sample of vulcanized rubber at 100° C, the curve of f/f_0 as a function of time was constructed, where f/f_0 is the ratio of the stress f at constant elongation at time t and with an initial stress f_0 . In these experiments, the elongation was 50 per cent.

According to the theory of Tobolsky⁶, the decrease in this ratio is caused solely by the action of oxygen. This latter action was followed spectroscopically. The experiments showed that, to be able to follow, for example, by studying the C=O or OH bands, in which case even the first stages of oxidation influence considerably the mechanical properties, it is necessary to use test-specimens of such thicknesses that the losses of radiation, notably by diffusion, become so great that quantitative results are impossible.

Figure 5 shows for one individual sample of vulcanized rubber (a) the relaxation curve, and (b) the extinction curve for the C=O group. The extinctions are plotted with increasing values upward (curve b), but the f/f_0 values are, to make a clearer comparison, plotted with increasing values downward (curve a).

The measurements of the extinction were obtained with a sample reduced to powdered form, which was heated under the same conditions as those for the ring test-specimens which were tested in the tensometer.

It was possible to measure spectroscopically the chemical changes only at and beyond the stage where the mechanical properties had already been profoundly altered. However, these are only preliminary experiments, and it seems reasonably certain that the spectroscopic technique can be improved, particularly with respect to the preparation of samples. Nevertheless, there is no doubt that the rheological properties of rubber are affected in a very sensitive way by extremely small chemical changes which are difficult to detect by ordinary chemical or physical methods. In particular, the method of direct measurement of the total absorption of oxygen has not given satisfactory results⁷.

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- ⁵ The details of the calculations will be published elsewhere.
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X-RAY ANALYSIS OF THE MOLECULAR STRUCTURE OF RUBBERS. X-RAY DIFFRACTION OF AMORPHOUS RUBBER *

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CHANGE OF MOLECULAR STRUCTURE OF RUBBER AS A RESULT OF FATIGUE

The potentialities of x-ray analysis of the molecular structure of rubbers can be widely extended by measuring the intensities of the amorphous halo and continuous background of scattering in the diffraction patterns of unstretched test-specimens. This method can be applied to the study of the effect of repeated stretching of rubbers. Questions pertaining to the fatigue of rubbers have immense importance now in the performance of rubber products.

The methods of determining the crystallization of natural rubber and of measuring the intensity of the amorphous halo for synthetic rubber were employed for investigating the changes of the molecular structure of rubber due to repeated stretching¹.

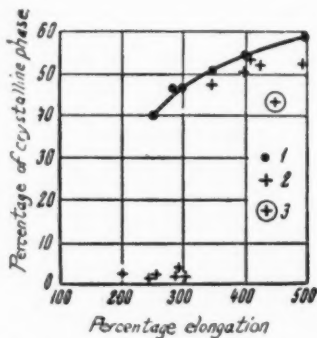


Fig. 1.—Decrease of crystalline phase during fatigue of natural-rubber vulcanizates. 1. Unfatigued. 2. After 10,000 cycles. 3. After 1,000,000 cycles.

The crystallization of raw smoked-sheet rubber decreased as a result of fatigue; a similar phenomenon was observed for its vulcanizates. The vulcanizates which were stretched less than 300 per cent lost their crystallization property altogether after fatigue, and, at greater elongations, the content of the crystalline phase greatly decreased (see Figure 1).

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Bulletin of the Academy of Sciences of the USSR, Physics Series*, Vol. 15, No. 2, pages 209-17 (1951). The first part of this paper outlines work already published in nearly the same form (see Kasatochkin and Lukin, *RUBBER CHEMISTRY AND TECHNOLOGY*, Vol. 24, No. 4, pages 763-766, October-December 1951) and is omitted from this translation.

The decrease of crystallization in the fatigued specimens was accompanied by a decrease of moduli (stresses measured at 200 per cent elongation by a Scott apparatus). The phenomena observed are in accord with existing theories about the fatigue process, together with the chemical processes involved in the oxidation of rubber.

We observed interesting changes of intensity of the amorphous halos for x-ray diagrams taken of fatigued specimens of vulcanized sodium-butadiene rubber. In order to obtain quantitative measurements, we measured the intensity of the amorphous halo by comparing it to a standard.

The x-ray diagrams were taken for specimens stretched 240 per cent.

In Figure 2, curve 1 represents the intensity of the amorphous ring of unfatigued specimens, and curve 2 represents that of specimens after 10,000 cycles. As is seen in the figure, as a result of fatigue the intensity of the amorphous ring sharply increased.

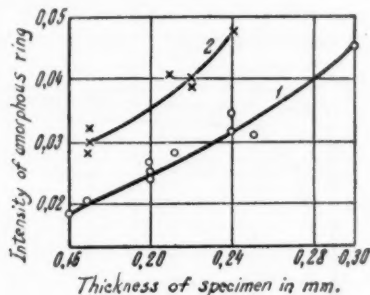


Fig. 2.—Change of intensity of amorphous ring during fatigue of vulcanizates of sodium-butadiene rubber. 1. Unfatigued. 2. After 10,000 cycles.

In the x-ray diagrams for fatigued specimens, no uniformity of intensity is observed around the amorphous ring. The observed increase of intensity of the amorphous ring as a result of fatigue can be explained on the basis of previous observations of the molecular structure of the amorphous phase of the rubber.

We observed that the proportion of the gaseous and liquid phases of the amorphous rubber changes during different processes. During fatigue resulting from mechanical action and the formation of oxygen-bearing polar groups by oxidation of the rubber, an increase of intermolecular energy takes place, and this leads to a decrease of the molecularly disordered phase of the substance, and, consequently, to an increase of intensity of the amorphous ring in the diffraction picture.

Thus the nature of aggregation of the molecular chains changes during fatigue.

INVESTIGATION OF THE CRYSTALLIZATION OF LOADED VULCANIZED RUBBERS

Observation of the crystallization of natural rubber during stretching made possible a detailed investigation of its molecular structure and the establishment of a connection between its tendency to crystallize and certain of its physical-mechanical properties. The study of rubbers during processing and their behavior in service are of great practical interest.

The results of an x-ray investigation of the crystallization of loaded rubbers, made earlier² in connection with a study of the mechanism of tensile strength and molecular changes in rubber during vulcanization, enable us to pass on to the study of loaded industrial rubbers.

The mechanism of reinforcement and the specific effect of various fillers is one of the most fundamental and practical questions of rubber technology.

The ratio between the intensity of the amorphous halo and the intensity of the crystalline reflection of a stretched specimen of vulcanized rubber indicates its crystallizing property and permits a measurement of the relative amount of the crystalline phase in different specimens. As was shown earlier in an investigation of the vulcanization process³, the curve of crystallization (amount of crystalline phase vs. time of vulcanization) quite fully reflects the molecular mechanism of vulcanization and indicates the most important physical-mechanical properties of vulcanizates. For example, the course of the curve of tensile strength with respect to the time of vulcanization almost coincides with the crystallization curve. The presence of an active filler in a vulcanized rubber mixture essentially changes the nature of its crystallization curve.

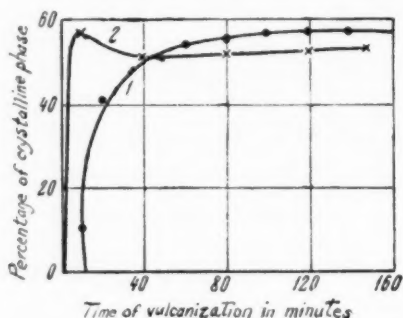


FIG. 3.—Crystallizing property of natural rubber at different stages of vulcanization (elongation 400 per cent). 1. Unloaded mixture. 2. Mixture loaded with 30 parts by weight of carbon black.

In Figure 3 are shown the crystallization curves of specimens containing 30 parts by weight of channel carbon black, and, for comparison, curves of samples of an unloaded mixture of the same composition. The composition of the mixture, by weight, was smoked sheet 100; sulfur 5; zinc oxide 5; and stearic acid 2 parts.

For the loaded mixture, the crystallization maximum was found in the short time range of vulcanization, and the induction period (the vulcanization time before crystallization) sharply decreased. The induction period of unloaded mixtures is characterized by the accumulation of a modicum of chemically combined sulfur, which can form a general spatial network of the molecular chains of the rubber by uniting the chains by sulfur bridges.

The relation of the proportion of crystalline phase to the chemically combined sulfur, shown in Figure 4, indicates, however, that for mixtures containing carbon black, crystallization begins when the amount of combined sulfur is still extremely small; in fact, the amount of crystalline phase reaches a maximum even before the beginning of crystallization in unloaded rubber mixtures.

When a sufficiently large quantity of filler (carbon black) is present, unvulcanized mixtures are also capable of crystallizing during stretching. These

rubbers do not crystallize at all without such a filler. Furthermore, loading sharply decreases the elongations which are necessary for crystallization to begin (for loaded rubbers, 175 per cent, and for unloaded rubbers, 300 per cent).

The x-ray diffraction diagrams of stretched specimens of loaded vulcanizates, as distinguished from those of unloaded specimens, are spread out along the azimuth, due to the shape of the interference spots and to the increased sharpness of the interferences with higher indexes. These differences, substantial in the initial stages of vulcanization, become minimized as vulcanization progresses.

The changed character of the crystallization curve and diffraction pattern attest to the fundamental influence of an active filler on the vulcanization process, and can be explained by the effect of the adsorption of the molecular chains of the rubber on the surface of the filler particles.

The azimuthal extension of the interference spots by the addition of a filler is the result of the deviation of the axes of the rubber crystals away from the direction of stretching of the specimen, and is a direct proof of the union of the

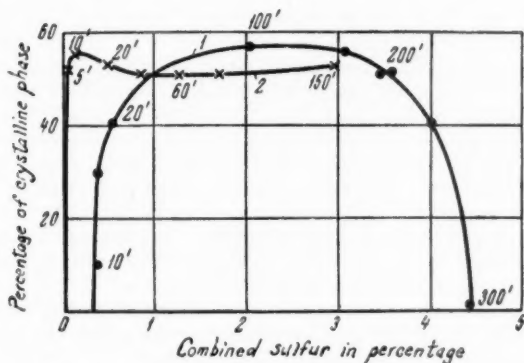


FIG. 4.—Relation between the crystallizing property of vulcanized natural rubber and its content of combined sulfur (elongation 400 per cent). 1. Unloaded mixture. 2. Mixture loaded with 30 parts of channel carbon black.

rubber crystals with the filler particles. The sharper and more nearly uniform interference spots with higher indexes during the initial stages of vulcanization must be caused by the relatively large size of the crystals.

The crystallization of loaded carbon black-rubber mixtures without a vulcanizing agent (sulfur), as well as the shortening of the period of induction and the displacement of the maximum on the crystallization curve into the lower time ranges, is also explained by the adsorption of the molecular chains on the surface of the carbon black particles.

A necessary condition for the crystallization of rubber, as follows from previous investigations³, is the formation of a molecular network structure which can apply pressure to the entire volume of the stretched specimen. In vulcanized rubber, the presence of such a network is provided by the sulfur bridges, which firmly unite the molecular chains with valence bonds. During the crystallization of rubber mixtures loaded with carbon black but containing no sulfur, the bond between the molecular chains which is necessary to the formation of a spatial network is formed by the adsorption forces of chain segments

on the surface of the filler particles. For a more detailed explanation of the molecular mechanism of crystallization on the basis of the results obtained by our x-ray investigation, it is necessary to account for the straightening of the adsorbed molecular chains caused by the loss of freedom of rotary motion of the individual links.

Fixation on the flat crystalline surface of the filler particles of two or more spatially identical atoms or atomic groups will necessarily lead to a straightening of the chain; this can be considered to be one-dimensional crystallization. The probability of formation of two-dimensional crystals is also very great in this case.

Not only the individual straightened chain segments, but also groups of such segments, serve as nuclei of crystallization during stretching of specimens of loaded vulcanized rubbers. Only those adsorbed segments of the chains, however, whose direction coincides with that of the internal forces or forms a small angle with them, as would follow from the relatively small length of the elongated interference spots on the x-ray films, can serve as centers of crystallization.

In addition, the theory which we elaborated concerning the mechanism of crystallization of loaded vulcanizates can also serve to explain their behavior with respect to mechanical properties. The presence of a filler in a vulcanizate causes a more nearly uniform spatial distribution of stresses in the specimen.

When vulcanized rubber is deformed, the chain segments which are subjected to deformation are, because of being united by weak adsorption forces on the surface of the filler particles, broken from the surface of the filler particles, while at the same time the undeformed chain segments are adsorbed on the surface of the filler particles. Aleksandrov⁴ ascribes to the rubber crystals a role similar to that played by reinforcing pigments. The analogy is complete if we consider that, in both cases, the molecular chains are oriented and straightened, and the intermolecular forces are identical.

The increase of the modulus of unloaded vulcanizates with increase of the proportion of combined sulfur is attributable principally to the increased rigidity of the same molecular chains of the rubber.

The primary cause of the rigidity of a molecular chain of vulcanized rubber is the fixation of the links by the sulfur bridges, which causes a doubling of each chain segment at the point of fixation as a result of the loss of freedom of rotation of a fixed link. In loaded vulcanizates, the links of the molecular chains of rubber are fixed by the adsorption forces on the surface of the filler particles. Such a fixation of links naturally causes an increase of the length of the segments at the points of fixation of the chain segments and a general increase of rigidity of the molecular chains and, consequently, an increase of the modulus of the vulcanizate. We may assume that the length of a segment during the adsorption of the chains on the surface of the filler particles is double the length of a segment of a free molecular chain and the length of the adsorbed particle itself.

The orienting action of the adsorbing surface of the filler particles reduces the amount of work necessary to orient the molecular chains during the formation of a rubber crystal and causes a noticeable decrease of the critical elongation which is necessary for the commencement of crystallization of loaded vulcanizates.

It is necessary to note that the correction for the volume occupied by the filler in the mixture by no means accounts for the observed decrease of the critical elongation at which crystallization begins, nor for the modulus of a

loaded vulcanizate in comparison with that of a corresponding unloaded vulcanizate.

INVESTIGATION OF THE MOLECULAR ORIENTATION OF LOADED VULCANIZATES OF SYNTHETIC RUBBER

Many rubber products at the present time are prepared from synthetic rubbers. In distinction from natural rubber, these rubbers do not crystallize during stretching. Structural investigations of synthetic rubbers required the development of special x-ray methods. With the aim of studying the changes of molecular structure and of physical-mechanical properties of vulcanized synthetic rubbers in relation to the important questions of vulcanization and loading, the method⁵ of determining the molecular orientation worked out by one of the authors was used.

The study of molecular orientation during stretching has been handicapped until now by the absence of any direct methods of measuring such orientation.

Orientation of the molecular chains of vulcanized natural rubber can be observed up to the beginning of crystallization⁶. In the process of stretching, right up to the appearance of crystals, the relative intensity of the amorphous ring increases in the region of the equator. In ordinary vulcanized rubber, crystallization begins before any nonuniformity is noticeable in the halo. We prepared vulcanizates containing by weight 100 parts of smoked-sheet rubber, 7 parts of sulfur, and 0.8 part of tetramethylthiuram disulfide (vulcanization time 300 minutes), which began to crystallize only at the highest elongations, i.e., about 600–700 per cent, whereas ordinary vulcanizates crystallize at elongations of 200–300 per cent. At lower elongations, the amorphous ring has two intensity maxima; for example, at 500 per cent, the intensity on the equator exceeds the intensity at the meridian by more than 50 per cent. The appearance of crystals is accompanied by the disappearance of the nonuniformity in the amorphous halo.

The nonuniformity of the amorphous halo is also observed in the x-ray patterns of stretched non-crystallizing vulcanizates of butadiene-styrene rubber. Thus, the equatorial maxima can serve as a means of studying the orientation properties of rubbers.

The method of measuring molecular orientation is the following:

The x-ray diagrams are photometered along two perpendicular directions, the meridian and the equator. If the smaller meridional intensities are taken as 100, then the greater intensities along the equator are a measure of the degree of orientation.

The final calculation is made according to the equation:

$$\text{degree of orientation} = \left(\frac{a}{b} - 1 \right) \cdot 100,$$

where a is the intensity of the amorphous ring at the equator, and b is the intensity at the meridian.

This method of measuring the molecular orientation was widely used in the study of vulcanized butadiene-styrene rubbers. The change of the orientation of rubbers was determined in connection with the investigation of the mechanism of tensile strength, during an investigation of the vulcanization process, fatigue during multiple deformations, the specific properties of various softeners, etc.

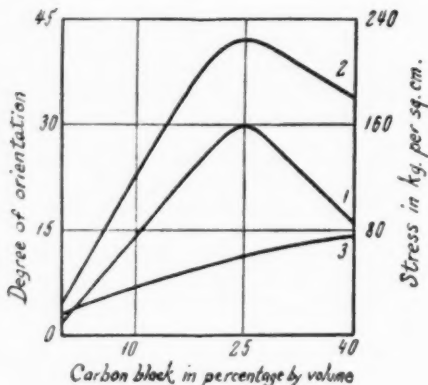


Fig. 5.—Changes of properties of vulcanized butadiene-styrene rubber with increase of loading of channel carbon black. 1. Degree of orientation at 200% elongation. 2. Tensile strength. 3. Modulus at 200% elongation.

Unloaded rubbers have a slight tendency toward orientation and relatively low tensile strengths (see Figure 5, curves 1 and 2). With loadings up to 25 parts by volume (45 per cent by weight), orientation increases linearly. At the highest loadings of channel carbon black, the orientation decreases. The maximum of the orientation curve occurs at the loading of 45 parts by weight, which is similar to the loading frequently used in practical recipes. The course of the orientation curve is similar to that of the tensile strength curve.

The values of the moduli increased linearly with increase of filler content (see Figure 5, curve 3). The character of the orientation curve does not correspond with that of the modulus curve.

The similarity in the character of the orientation curve and that of the tensile strength curve graphically illustrates the molecular mechanism of tensile strength.

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INFRARED ANALYSIS OF RUBBER DERIVATIVES *

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This paper is a continuation of our studies on rubber derivatives, which were surveyed in a previous communication¹. The scientific purpose of those studies is to elucidate the correlation between structure and mechanical properties of polymers derived from natural and synthetic rubber², while the technological aim is to produce plastics from rubber³.

Identification of halide structures in rubber derivatives has been achieved by kinetic analysis with organic bases⁴. The nature of certain double bonds can be established kinetically using perbenzoic acid as a reagent⁵, and additional information on double bond structure can be gained from the course of reaction with ICl^6 and, finally, with HCl^7 . These methods are, however, useless in the study of unsaturation of halogenated polymers, as the double bonds in many olefinic halides are not reactive at all with these reagents. We decided, therefore, to explore the possibilities of infrared analysis as an analytical tool. Evidence for the migration of double bonds in thermally degraded rubber, in chlorinated rubber, and in vulcanized rubber has been previously reported briefly by Sheppard and Sutherland⁸.

In addition to the double bond problem, it was hoped to gain some semi-quantitative information on the remaining number of unchanged methyl groups in certain rubber derivatives.

EXPERIMENTAL

The spectrometer used was a single-beam instrument with Wadsworth-mirror, rock-salt prism, and photographic registration. A Globar was used as a source of radiation. Spectra were measured between $5.7\text{--}14\ \mu$.

Methods applied for preparing chlorinated rubber⁹, hydrochlorinated rubber¹⁰, and cyclized rubber¹¹ have been extensively discussed elsewhere. Chlorinated rubbers of low chlorine content were fractionated sharply and analyzed immediately after preparation when the amount of oxidation, deduced from the intensity of the C=O bond, was still small. Details of the preparation of rubber-silver salt complexes will be published later. Films were prepared from chloroform solutions on glass or rock-salt plates, the former being measured as a free film on a metal frame. The thickness d of the films, measured with a micrometer, varied between 30 to $150 \times 10^{-4}\text{ cm}$.

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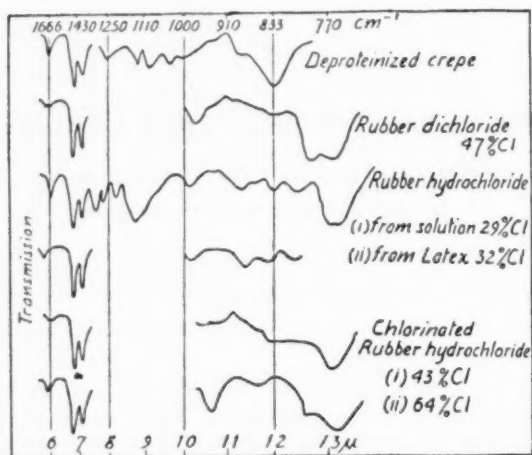


Fig. 1.—Spectra of rubber, rubber chlorides and rubber hydrochlorides.

The curves of the transmission T and the extinction coefficient k , where $k = (1/d) \log 1/T$, as a function of wave length were derived in the ordinary way from the curves of transmitted and incident energy and the energy transmitted through the blank NaCl plate, the scattering being very low. As the intensity of a characteristic bond we took the difference of the maximal value of absorption and its value at the lowest neighboring minimum.

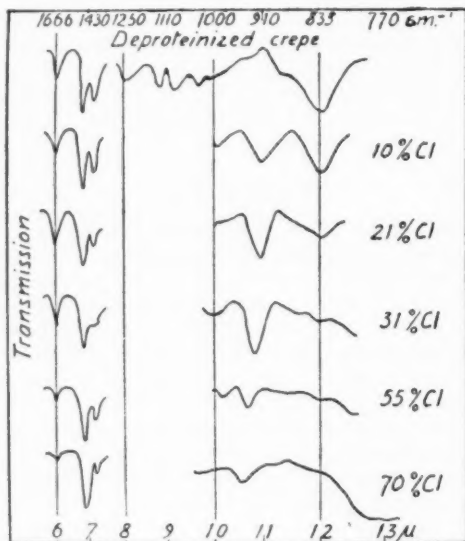


Fig. 2.—Changes in the spectrum of rubber during the course of chlorination.

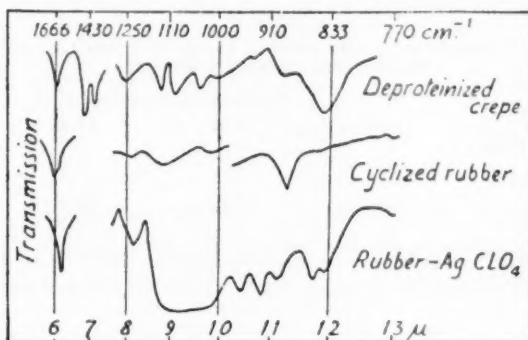


FIG. 3.—Spectra of rubber and some rubber derivatives.

Some representative spectra of rubber and rubber derivatives are reproduced in Figures 1, 2, and 3. The extinction coefficients derived from these figures are summarized in Tables I and II and Figures 4 and 5. Most of the points given

TABLE I

DOUBLE BOND AND METHYL GROUP INTENSITIES OF RUBBER, RUBBER HYDROCHLORIDE, RUBBER DICHLORIDE, AND CHLORINATED RUBBER HYDROCHLORIDE

Polymer	% Cl	Relative % of double bonds	$k_{6\mu}$	$k_{10.3\mu}$	$k_{10.8\mu}$	$k_{11.2\mu}$	$k_{11.9\mu}$	$k_{\text{CH}_3/\text{CH}_2}$
Hydrochlorination of Rubber								
Natural rubber from latex	0	100	55	0-20	0-10	30	160	0.45
Rubber—HCl from solution	29	20	30	30	0	50	50	0.75
Rubber—HCl from latex	32	10	0-8	20	0	40	40	0.75
Addition of Chlorine to the Double Bond								
Natural rubber from latex	0	100	55	0-20	0-10	30	160	0.45
Rubber dichloride from solution	38	42	20	40	15	0	20	0.70
Rubber dichloride from solution	44	25	5	30	45	0	15	0.70
Rubber dichloride from solution	47	15	15	45	15	0	25	0.70
Substitution of Hydrogen by Chlorine in Rubber Hydrochloride								
Rubber—HCl from solution	29	20	30	30	0	50	50	0.75
Chlorinated rubber—HCl	43	?	10	15	15	0	0-10	0.65
Chlorinated rubber—HCl	56	?	0-5	15	35	0	0	0.70
Chlorinated rubber—HCl	64	?	0-5	15	50	0	0	0.75

TABLE II
INTENSITIES OF THE DOUBLE BOND IN RUBBER AND
RUBBER-SILVER SALT COMPLEXES

Polymer	Position in μ and intensities of the bands			
Natural rubber	6.00 m.	10.30 v.w.	11.25 w.	11.9 v.s.
Complex with 19.8% AgNO_3^a	6.11 s.	10.25 w.	11.14 s.	11.0 v.s'
Complex with 41.3% AgClO_4^b	6.14 v.s.	10.38 s.	10.9 v.s.	11.9 w.
			11.14 s.	

v.s., very strong; s, strong; m, medium; w, weak; v.w., very weak.

^a 0.1 mole AgNO_3 /1 mole C_5H_8 . A broad band in the region between 6.9-7.9 μ is due to the nitrate group.

^b 0.23 mole AgClO_4 /1 mole C_5H_8 . A broad band in the region between 8.8-9.9 μ is due to the perchlorate group.

in Figures 4 and 5 were measured on two different films from the same product. Data for rubber refer to three different samples, and those for rubber hydrochlorides and rubber chlorides to 2-5 samples prepared independently.

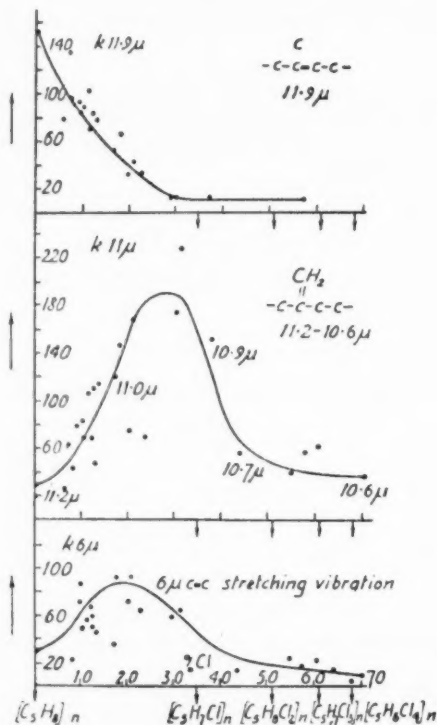


Fig. 4.—Influence of the degree of chlorination on the double bond intensities in chlorinated rubber.

These results are discussed in the order of increasing complexity of the chemical problem.

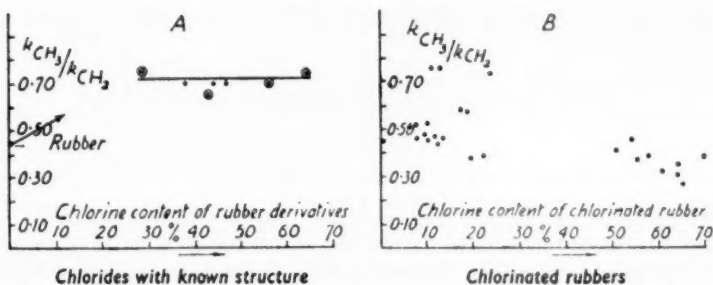
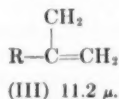
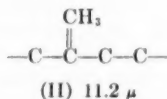
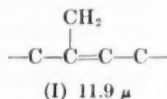


Fig. 5.—Relative intensities k_{CH_3}/k_{CH_2} of the methyl groups in chlorine-containing rubber derivatives. ● Rubber dichlorides; ○ Rubber hydrochlorides and chlorinated rubber hydrochlorides.

RESULTS

THE DOUBLE BOND FREQUENCIES IN RUBBER AND RUBBER DERIVATIVES

Rubber.—The intensity of the $6.0\ \mu$ $C=C$ stretching frequency is nearly the same for a number of samples, but it changes as the rubber becomes oxidized. The intensity of the $11.9\ \mu$ band is much stronger and typical of the $RRC=CHR$ group. A weak band at $11.2\ \mu$, typical of a vinyl group has been observed already by previous workers¹², who assigned its occurrence tentatively to end groups in the rubber chain (III). In our view, the vinyl group would be also consistent with the structure (II), which could occur in small or larger quantities within the chain.



This band at $11.2\ \mu$ shifts on chlorination to shorter wave length and is finally found at $10.6\ \mu$ at a chlorine content of 70 per cent. We shall call this band in rubber and its derivatives the $11\ \mu$ band.

Finally, there is a weak band at $10.3\ \mu$ which has been identified in other polymers¹³ and in many other substances with the *trans*-configuration of the double bond. It has been observed by us, as well as by others⁸, in some samples of rubber as a very weak band which is stronger in certain derivatives (see Figures 1 and 2) and in ebonite⁸.

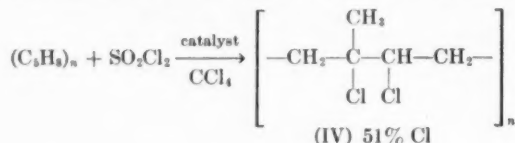
Rubber hydrochlorides.—The addition of HCl to rubber in solution and in latex occurs with great ease. It is difficult to saturate all double bonds, although the theoretical figure has been approached in some experiments starting from latex¹⁰. The products prepared from solution are saturated to 80 per cent, but the intensity of the $6\ \mu$ band does not differ essentially from that of the original rubber (see Table I and Figure 1).

Those substances made from latex are saturated to 90 per cent and show no absorption at $6\ \mu$, while the presence of residual unsaturation is indicated by a weakened $11.9\ \mu$ band. This indicates that small changes in the structure can cause great differences in the $6.0\ \mu$ intensity.

Rubber chlorides.—The addition of chlorine to the double bond can be achieved with SO_2Cl_2 and a source of radicals¹⁴.

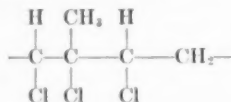
Substitution leading to the formation of allyl chlorides occurs, however, as a side reaction. The amount of allylic groups can be estimated from the reac-

tion with aniline. Nothing was known about the possible shift of double bonds

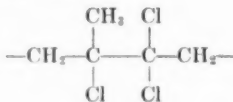


in the course of the reaction with radicals. Infrared analysis (Table I and Figure 1) confirms the existence of residual double bonds, some of which must be of the original structure (11.9μ band), while a somewhat irregular increase of the 10.3μ and 10.8μ intensities indicates the presence of isomerized and migrated double bonds.

Chlorinated rubber hydrochlorides.—A product similar to this rubber dichloride is obtained from the reaction of rubber hydrochloride with chlorine activated by light. The substitution leads first to the transformation of the tertiary chloride into a dichloride at a chlorine content of about 50 per cent and can be continued to 70 per cent chlorine content. The chemical evidence, therefore, points to the structures (IV), (V), and (VI).



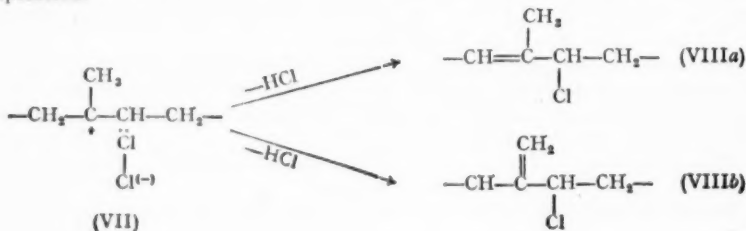
(V) 61% Cl



(VI)

Nothing is definitely known about the formation of new double bonds or of C—Cl₂ groups in the course of this smooth chlorination reaction. Stability is, however, considerably higher than that of the corresponding chlorinated rubbers with 50–60 per cent chlorine. The absence of the 11.9μ band excludes the occurrence of the original double bond, but the increase in intensity of the 11μ band is consistent with a possible formation of small quantities of allylic groups (Table I and Figure 1).

Chlorinated rubber.—It is known from extensive studies in this field that the interaction of chlorine and rubber in solution, as well as in latex, first leads to the formation of allylic chlorides, which are gradually transformed into polychlorides. The latter process can occur either by addition of chlorine to the double bond of the allylic chloride or by continuous substitution leading to polychlorinated olefins. The vigorous beginning of the reaction makes the production of a homogeneous derivative difficult, and the following results refer, therefore, always to fractionated chlorinated rubber obtained by gradual precipitation.

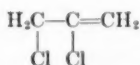


Chemical evidence makes an ionic mechanism probable¹⁵. The hypothetical intermediate (VII) can lead to two different types of allylic chlorides (VIIIa) and (VIIIb). A decision between (VIIIa) and (VIIIb) could be made by infrared analysis. The double bond absorption of (VIIIa) should be found near the original 11.9 μ band, that of (VIIIb) near the 11.2 μ band. Figures 2 and 4 allow one to draw the following conclusions.

(1) The original 11.9 μ band shows a weakening in intensity even in the first phase of the chlorination; it practically disappears when one atom of chlorine has been substituted in each isoprene unit. This makes formula (VIIIa) improbable.

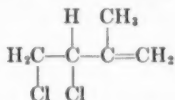
(2) The weak 11 μ band of rubber shifts to a shorter wave length in the derivative. The intensity of this 11 μ band becomes of the same order as that of the original strong 11.9 μ band at the chlorination phase of $(C_5H_7Cl)_n$. This result is consistent with formula (VIIIb).

The shift to the original 11.2 μ band to 10.9 μ on chlorination has been observed by us also in the following two reference compounds (IX) and (X).



Maximum at 11.05 μ .

(IX)



Maximum at 10.85 μ .

(X)

Moreover, Barnard, and his coworkers¹⁶ found a similar change on introduction of a chlorine atom.

This shift of the original 11.2 μ band to higher frequencies is continued on further chlorination of the rubber. The points at 50–70 per cent chlorine content in Figure 4 refer actually to absorption maximum at 10.7 μ . The observed intensity of this band decreases with the introduction of two or three chlorine atoms until it has reached the original low value. It is, however, not of zero intensity, indicating that some double bonds are left even in highly chlorinated rubber.

(3) The intensity of the 6.0 μ band increases with increasing chlorine content up to 30 per cent chlorine. This increase might be due to a shift of the double bond resulting in the formation of vinyl groups as derived from the behavior of the 11 μ band. But it should be borne in mind that the attachment, especially of polar groups, to a bond may also greatly change the intensity of the characteristic absorption band, due to a change in the effective dipole moment associated with the oscillation. However, the fact that the 6.0 μ band is persistent even in highly chlorinated rubbers proves the occurrence of residual double bonds, and so confirms the conclusions drawn from the behavior of the 11 μ band.

(4) Support for the assumption of formula (VIIIb) is also obtained from changes in the 7.25 μ CH_3 band. At 30–40 per cent chlorine content, the original sharp methyl band is disfigured into almost a shoulder, by an additional absorption in the transparent region between the absorption bands at 7.25 μ and 6.85 μ (see Figure 2). This might indicate that the absorption is due to the ethylenic CH -deformation frequency at 7.1 μ . Actually the CH_3 intensity cannot be measured in these fractions of the chlorination product; it reappears

with a reduced intensity in chlorinated rubber containing 40–70 per cent chlorine (see Figure 5B).

Cyclized rubber.—Cyclization is a polar polymerization reaction catalyzed by Lewis acids. The first phase must be a polarization of double bonds, which does not differ in principle from that of the assumed intermediate structure (VII) in chlorination. An analogous double bond shift could, therefore, be expected. An increase in intensity at the $11\ \mu$ band, together with a decrease at the $11.9\ \mu$, has already been observed by Sears¹⁷.

We have measured four samples of cyclized rubber prepared from latex¹¹ with an approximate loss of 50, 70 and 80 per cent of the original unsaturation, and have found in all samples a strong band at $11.2\ \mu$ and only a weak $11.9\ \mu$ band (see Figure 3). The chemical evidence points also to two types of double bonds, which differ measurably in their ease of reaction with HCl ¹¹.

Complex compounds with silver salts.—Chemical evidence led us to the assumption that the dissociation of crystalline complexes between silver nitrate or perchlorate and rubber was completely reversible. Some preliminary measurements of the spectra (see Table II and Figure 3) indicate, however, a decrease of intensity of the $11.9\ \mu$ band, whereas the $11\ \mu$ and $10.3\ \mu$ region increase both markedly in intensity. This suggests the occurrence of *cis-trans*-isomerization and of a double bond shift. Moreover, the $6.0\ \mu$ $\text{C}=\text{C}$ stretching vibration band is shifted to $6.1\text{--}6.2\ \mu$ and becomes much stronger, indicating a weakening of the $\text{C}=\text{C}$ bond due to the formation of π complexes. A study of the rubber regenerated from the complex is under way.

Intensity of the CH_3 deformation frequency at $7.25\ \mu$.—In this section the term relative intensity of the CH_3 band refers to the ratio:

$$k_{\text{CH}_3}/k_{\text{CH}_2} = k_{7.25\mu}/k_{6.85\mu}.$$

Measurements on a number of paraffinic reference compounds as well as data from literature make clear that this relative intensity is not independent of the rest of the molecule. Introduction of 2 or 3 neighboring chlorine atoms leads generally to a reduction of the CH_3 intensity. A decrease in intensity on chlorination is, therefore, not a direct measure of a reduced number of CH_3 groups. Unfortunately our reference data are not sufficiently extensive to discuss fully the changes in relative intensity observed on HCl or Cl_2 addition to the double bond of rubber. It is seen from Figure 5A that these reactions cause, not a decrease, but a marked increase in the $k_{\text{CH}_3}/k_{\text{CH}_2}$ intensity, which remains apparently unchanged on further chlorination of the hydrochloride. We do not yet know the influence of double bonds and the difference between $-\text{CHCl}-\text{CHCl}-$ and $-\text{CH}_2-\text{CCl}_2-$ groups in relation to the $7.25\ \mu$ band, which effects may partly compensate each other. A comparison of Figure 5A, and 5B reveals immediately that an essential difference exists between the controlled addition and substitution reactions (5A) and the complicated reaction products of direct chlorination (5B). The points in Figure 5B refer to the same fraction as those in Figure 4. It has already been mentioned that the original $7.25\ \mu$ band disappears in chlorinated rubber with 30–40 per cent chlorine content. Only a few of the other fractions indicate a stronger relative intensity, most of them are unchanged or show a decrease. The ratio 0.4 for the highly chlorinated products in Figure 5B should be compared with the ratio 0.7 obtained for products with similar chlorine content in Figure 5A. The loss of methyl groups on direct chlorination is tentatively suggested from these data. Methyl groups could disappear either by chlorine addition at the intermediate

(VIIIb) or by direct chlorination leading to the primary $R-CH_2Cl$ group. A search for the corresponding $C-Cl$ frequency is now being made.

DISCUSSION

Our data suggest that the intermediate formation of the vinyl configuration

$$\begin{array}{c} CH_2 \\ || \\ -C-C-C- \end{array}$$

by a shift of the original double bond occurs, not only in the course of chlorination reactions, but also in other reactions of rubber with acceptor molecules. The vinyl group in turn leads to a relative increase in the intensity of the 6.0μ $C=C$ stretching vibration, so that the latter becomes useless for even a rough estimate of double bond concentration in a polyisoprene derivative. The curious observation, that a hydrochloride with 20 per cent of the original double bond number shows still a moderate 6μ absorption, while one with 10 per cent of double bonds¹¹ has no 6μ band, indicates that small differences can cause significant changes in the 6.0μ intensity. The 6.0μ frequency is, however, very useful for the qualitative indication of residual double bonds. We have shown that chlorinated rubber with 65–70 per cent chlorine content still contains some double bonds, while the unsaturation of fully sulfurized ebonite has been previously mentioned by Sheppard and Sutherland⁸.

The discovery of vinyl groups in rubber derivatives explains immediately many observations made by the first-named author and his colleagues in past years. It is well known that the strong cross-linking tendency of polybutadi-

enes is due to the presence of 15–20 per cent of vinyl groups $-C-C-C=CH_2$, which are more apt to polymerize than "internal" double bonds. A significant difference between natural rubber and all its derivatives is that the latter cross-link on the slightest provocation like synthetic rubbers. This has been found with partly chlorinated rubber, cyclized rubber, isorubber, partly hydrochlorinated rubber, and even with the silver salt complexes. Our infrared data suggest double bond shifts as the probable cause of these disturbing side reactions.

Our data as well as those of previous authors¹² are consistent with the assumption of 1–5 per cent of vinyl groups in rubber. Chemical evidence on the structure of rubber does not exclude such small quantities of vinyl groups. Vulcanization is partly a polar reaction, just as is chlorination, and thus might lead to an increase of the originally small number of vinyl groups. In one case at least this supposition is supported by experimental evidence; the vulcanization of rubber with S_2Cl_2 is accompanied by the formation of a strong 11.2μ band according to Thompson¹⁸. This method of cross-linking rubber differs, however, chemically from the technical vulcanization with sulfur.

No positive indication of similar changes on reaction either with sulfur alone or with a mercaptobenzothiazole-type of accelerated mix can be deduced from published data¹⁹. This, however, does not exclude double bond shifts and isomerization, especially under other conditions of technical vulcanization⁸. The occurrence of vinyl groups in raw rubber and intermediate double bond shifts deserve closer study in view of their importance in relation to the tendency of rubber to form cross-links during vulcanization.

The results of our attempts to measure the methyl groups are rather disappointing. It is obvious that the relative intensity of the CH_3 bending deformation can be increased, as well as decreased, by a combination of addition and substitution reactions. Therefore not more than a rough qualitative picture has been obtained.

Summing up, our impressions gained from these exploratory experiments are that infrared analysis is a useful but delicate tool in polymer chemistry. The discovery of intermediate processes by qualitative observation of new frequencies can stimulate the work of technologists, but any attempt to draw semiquantitative conclusions from intensity measurements must be preceded by a detailed knowledge of the chemistry involved.

SUMMARY

Changes in the intensity of the double bond frequencies ($6.0\ \mu$, $10.3\ \mu$, $11\ \mu$, $11.9\ \mu$) and the CH_3 bending vibration occurring during the chlorination of natural rubber and the formation of various rubber derivatives have been studied. From the weakening of the original $11.9\ \mu$ bond and the appearance of a strong band at $11.2\text{--}10.9\ \mu$ it is concluded that a double bond shift in rubber occurs readily under the conditions of polar reactions:



The significance of vinylic groups for the aging properties of rubber derivatives is pointed out.

The intensity of the $6.0\ \mu$ $\text{C}=\text{C}$ stretching frequency cannot be used as a relative measure of unsaturation, as it depends on many other factors. It is, however, remarkable that chlorinated rubber with 70 per cent Cl has still a measurable absorption at $6\ \mu$.

The relative intensity of the $7.25\ \mu$ CH_3 bending vibration has been estimated from the $k_{\text{CH}_3}/k_{\text{CH}_2}$ ratio. Controlled addition of HCl or Cl_2 to the double bonds of rubber leads to an increased intensity at $7.25\ \mu$, while it is reduced in technical chlorinated rubber, of similar chlorine content.

ACKNOWLEDGMENT

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THE ACTION OF UNSATURATED COMPOUNDS ON NATURAL RUBBER IN SOLUTION. II. THE REACTION INDUCED BY HEAT ALONE *

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INTRODUCTION

In earlier investigations¹ the addition reaction of rubber, in 3 per cent benzene solution, with maleic *N*-methylimide in the absence of oxygen and in the presence of *p*-bromobenzoyl peroxide was studied. In this work, the relations existing, on the one hand, between the quantity of combined maleic *N*-methylimide and its initial concentration and, on the other hand, between the quantity of combined maleic *N*-methylimide and the initial concentration of *p*-bromobenzoyl peroxide were established.

The experiments showed that two different reactions take place; a rapid reaction initiated by the rapid decomposition of the peroxide, and then a slow reaction induced by heat alone. The relative rates of the two reactions were approximately 1 to 150-200.

Before studying the slow reaction, which may still to advantage be called the thermal reaction, it should be recalled that, among the various unsaturated compounds which are capable of combining with rubber, the choice fell upon maleic *N*-methylimide, for, in addition to its notable reactivity, it is stable, is relatively easy to prepare, and, above all, the proportion which combines with rubber can be determined directly by a simple nitrogen determination.

Finally it should be recalled that, when the reaction is catalyzed by a peroxide, there is evidence (1) of a chain reaction in which free radicals play a part, and (2) that the structures of the addition products correspond to the fixation of maleic *N*-methylimide, not by the ethylenic bonds of the rubber, but by the α -methylenic carbon atoms of the rubber, in accordance with the hypothesis advanced by Farmer².

After having described the experimental technique, attempts which were made, by means of a study of the kinetics of the reaction, to explain its mechanism will be described, and it will be shown that this mechanism is so complicated that a satisfactory mathematical interpretation was not possible. This in turn made it necessary to have recourse to a less theoretical method of attack by studying the rate of fixation of maleic *N*-methylimide by the rubber as a function of the temperature. Finally it will be shown how measurements of the unsaturation of the addition products make possible an interpretation of the structure of these products, as well as a hypothetical mechanism to explain their formation.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Bulletin de la Société Chimique de France*, 1951, Nos. 9-10, pages 773-778. Part I of this work was first published in the *Revue Générale du Caoutchouc*, Vol. 26, No. 6, pages 426-432, June 1949, and later in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 25, No. 1, pages 74-88, January-March 1952.

EXPERIMENTAL TECHNIQUE

In order to operate under as strictly controlled conditions as possible, the methods which had been used so successfully in the earlier work were again employed.

The maleic *N*-methylimide was prepared by the reaction of anhydrous methylamine with maleic anhydride, with subsequent dehydration of the acid amide which is formed². As a source of rubber, pale crepe was extracted with acetone, then dissolved in petroleum ether, and finally precipitated by anhydrous ethanol. It was found that the reaction must be carried out in the complete absence of oxygen if reproducible results are to be obtained. In order to operate under such conditions, resort was had to the method which Moureu and Dufraisse⁴ had employed in their work on the autoxidation of acrolein. In principle, this involves carrying out the reaction in a sealed glass tube containing the rubber and other reagents. After evacuating the system to a pressure of 10^{-3} mm., benzene, which has been as completely freed of oxygen as possible, is introduced into the tube. The quantity of benzene introduced to reach the desired concentration is controlled by a reference mark, by means of which the flow of benzene can be stopped at the right moment by sealing the pointed end of the tube with a blowpipe. This reference mark indicates the volume at room temperature, which must be calculated by taking into account the thermal expansion of the benzene so that the actual volume of the benzene at the temperature of the reaction is such that the concentrations of the reagents are correct.

After the reaction mixture has been heated and cooled, the rubber derivative is precipitated from its solution by methanol, washed with methanol, roughly dried, redissolved in benzene, precipitated a second time by methanol, and finally dried for several days in a vacuum.

The reaction product is then analyzed for two properties: (1) for its nitrogen content (by the Kjeldahl method), and (2) for its iodine number (by solution in chloroform and the use of iodine monochloride in carbon tetrachloride solution).

In the earlier work attention was called to the fact that, when the reaction is catalyzed by a peroxide, gelation occurs under certain conditions. In the present experiments, no such phenomenon was observed; the reaction products in all cases remained completely soluble in benzene and, after purification and drying, they were obtained in forms varying from that of rubberlike substances to fibrous materials or white powders, depending on the proportion of ethylene derivative combined.

ATTEMPTS TO STUDY THE KINETICS OF THE REACTION AT 170° C

As is well known, kinetic studies of a large number of reactions of organic chemistry have served as a means of explaining the mechanism of the reactions and to draw interesting conclusions regarding the structures of the products formed. After having demonstrated that rubber is capable of fixing maleic *N*-methylimide by the action of heat and without the aid of a peroxide, it seemed that the mechanism of the reaction, in considerably simplified form, might likewise be explained by a kinetic study.

Since the reaction appeared to depend primarily on the temperature, the first effort was directed toward finding out to what extent the temperature influences the rate of the reaction, or, what amounts to almost the same, toward finding out what proportion of maleic *N*-methylimide has combined, at the end of a given time, at different temperatures.

With this in view, maleic *N*-methylimide, in the proportion of 0.375 gram-moles per isoprene group, was made to react with 6 per cent benzene solutions of rubber (this concentration was calculated at the different temperatures concerned) in the temperature range of 110° to 170° C. Figure 1 embodies the results obtained, and shows that the proportion of maleic *N*-methylimide which combined with the rubber was seven times greater at 170° than at 110° C.

In the study of the kinetics of the reaction which is now to be described, it was decided to adopt throughout the experiments the temperature of 170° C. Higher temperatures were avoided for fear of possible degradation when the time of heating was prolonged.

Let us now consider the equations which represent the rate of the reaction. If x is the number of maleic *N*-methylimide (mI) before any reaction with the β -isoprene groups of the rubber, the rate of the reaction at any instant t and at any constant temperature is represented by the equation:

$$V = k[\text{mI}]^{\alpha}[\text{rubber}]^{\beta} \quad (1)$$

where k is the rate constant, which depends on the temperature, and $[\text{mI}]^{\alpha}$ and

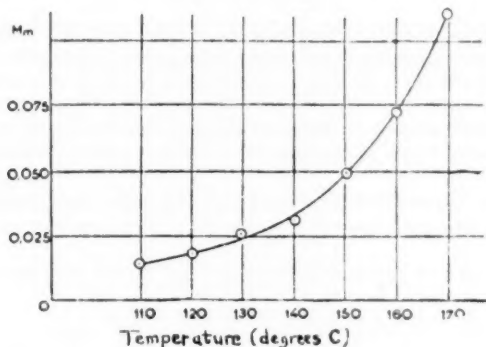


FIG. 1.—Quantity of maleic *N*-methylimide (Mm), in gram-moles per isoprene group of rubber, which combined in 75 hours, as a function of the temperature.

$[\text{rubber}]^{\beta}$ represent the concentrations of maleic *N*-methylimide and rubber, respectively.

Expressed otherwise:

$$\frac{dx}{dt} = k(a - x)^{\alpha}(b - x)^{\beta} \quad (2)$$

where a is the initial concentration of maleic *N*-methylimide, b is the initial concentration of rubber, and x is the concentration of maleic *N*-methylimide fixed at time t .

By varying a and b independently as a function of time and then determining x experimentally (by determining the N content of the addition product), it seemed possible to determine the values of α and β , i.e., to know the order of the reactions. Such information would be of much value in studying the mechanism of the reactions.

Two series of experiments were carried out, in which benzene solutions of different concentrations of rubber and of maleic *N*-methylimide in sealed

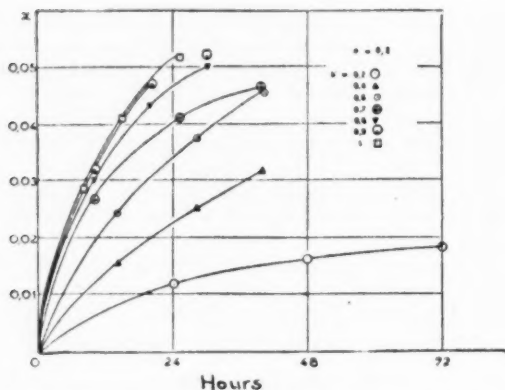


FIG. 2.—Quantity x (calculated as gram-moles per liter) of maleic *N*-methylamide which combined with rubber at 170° C, as a function of time, with an initial concentration, a , of maleic *N*-methylamide of 0.2 gram-mole per liter and concentrations, b , of rubber from 0.2 to 1 isoprene group.

tubes were heated at 170° C for different lengths of time. The reaction products were purified and dried, and their nitrogen contents were determined.

The concentrations a , b , and x were calculated in gram-moles per liter of solution; the concentration of rubber as the number of isoprene groups. In all cases, the concentrations per liter are those actually existant at 170° C, *i.e.*, with account being taken of the volume expansion of the benzene as a result of the heating.

In the first series of experiments, the initial concentration of maleic *N*-methylimide was kept the same, while that of rubber was varied.

$$a = 0.2, b = 0.2, 0.4, 0.6, 0.7, 0.8, 0.9, \text{ and } 1.$$

$$a = 0.3, b = 0.1, 0.2, 0.3, 0.4, 0.7, \text{ and } 1.$$

$$a = 0.4, b = 0.2, 0.3, 0.4, 0.7, \text{ and } 1.$$

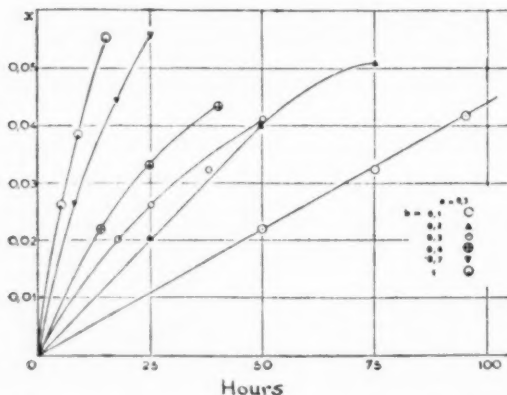


FIG. 3.—Quantity x (calculated as gram-moles per liter) of maleic *N*-methylimide which combined with rubber at 170° C, as a function of time, with an initial concentration, a , of maleic *N*-methylimide of 0.3 gram-mole per liter and concentrations, b , of rubber from 0.1 to 1 isoprene group per liter.

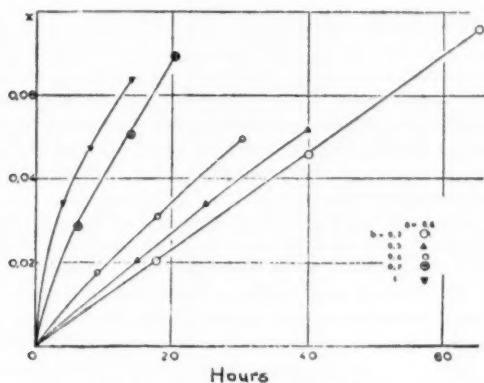


FIG. 4.—Quantity x (calculated as gram-moles per liter) of maleic N -methylimide which combined with rubber at 170° , as a function of time, with an initial concentration, a , of maleic N -methylimide of 0.4 gram-mole per liter and concentrations, b , of rubber from 0.2 to 1 isoprene group per liter.

In the second series, b was kept constant, and a was varied.

$$b = 0.4, a = 0.03, 0.1, 0.2, 0.3, 0.4, 0.7 \text{ and } 1.$$

$$b = 1, a = 0.1, 0.2, 0.3, 0.4, 0.7, \text{ and } 1.$$

The curves in Figures 2, 3, 4, 5, and 6 give a summary of the results obtained. It is obvious that, in some cases, these curves are practically straight lines.

Equation (2) gives, when $t = 0$, the initial rate V_0 :

$$V_0 = ka^ab^b \quad (3)$$

from which is derived, when a is constant (the curves of Figures 2, 3, and 4):

$$\log V_0 = K \log b \quad (4)$$

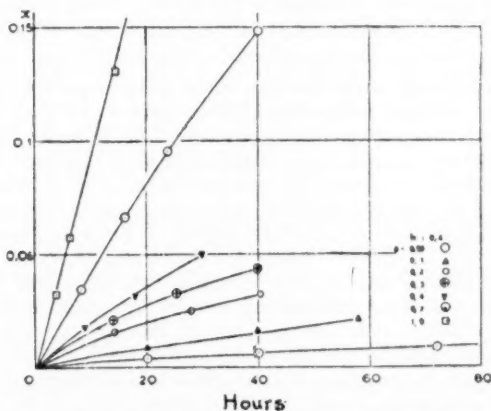


FIG. 5.—Quantity x (calculated as gram-moles per liter) of maleic N -methylimide which combined with rubber at 170° , as a function of time, with an initial concentration, b , of rubber of 0.4 isoprene group per liter and concentrations, a , of maleic N -methylimide from 0.03 to 1 gram-mole per liter.

and when b is constant (the curves of Figure 5 and 6):

$$\log V_0 = K'\alpha \log a \quad (5)$$

The only way to determine V_0 is to measure the slope at the origin of the tangents to the different curves; however, except in cases where the first part of the curves are practically straight lines, an exact tracing of these tangents is very difficult, and they are not shown on the curves because of the complicated appearance which would result.

To calculate α and β according to Equations (4) and (5), all that is necessary in principle is to plot the changes of $\log V_0$ as a function of $\log b$ and of $\log a$. If the points fall on a straight line, their slopes give the values of α and β , respectively. Actually an attempt was made to construct these curves, but the results were far from conclusive, and although the first three or four points formed an almost straight line, the other points departed appreciably from this straight line.

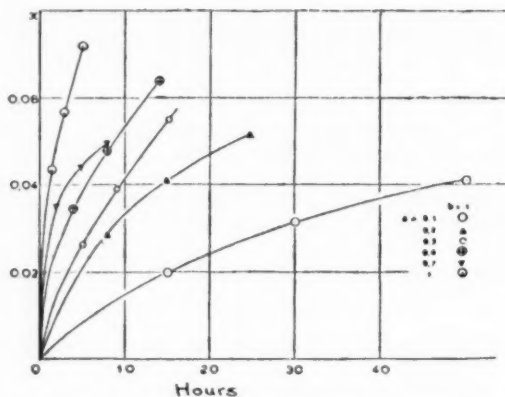


FIG. 6.—Quantity x (calculated as gram-moles per liter) of maleic N -methylimide which combines with rubber at 170° , as a function of time, with an initial concentration of rubber of 1 isoprene group per liter and concentrations, a , of maleic N -methylimide from 0.1 to 1 gram-mole per liter.

In summary, a study of the kinetics of the reaction gave no information of real value except perhaps verification of the expected fact that the rate varies qualitatively with the concentrations of rubber and of maleic N -methylimide and that the reaction must be more complicated than had been thought at the beginning of the work. In fact, various investigators who have carried out successful studies of the kinetics of macromolecular reactions have either worked with much simpler systems than natural rubber, or have employed much lower concentrations, and to follow closely the reactions, the use of continuous physical methods more precise than nitrogen determinations are necessary. Most important of all, these investigators worked at much lower temperatures than 170°C , at which point secondary reactions that are still uncertain and that may disturb the progress of the principal reaction are not at all impossible.

In the reactions concerned in the present work, therefore, rather unfavorable conditions were encountered, and, in addition, the rubber used in the experiments was certainly not strictly pure $(\text{C}_5\text{H}_8)_n$ rubber hydrocarbon. Different investigators who have studied the kinetics of the autoxidation of ole-

ins, such as cyclohexene, squalene, dihydromyrcene⁵, ethyl linoleate⁶, etc., which are very simple in comparison with the rubber hydrocarbon, have called attention to the numerous difficulties they encountered in purifying their products, despite the fact that these investigators had at their disposal processes such as molecular distillation which are inapplicable to rubber. It is then quite possible that, in the case of rubber, impurities of unknown origin act as true catalysts or inhibitors of the reaction. If so, this would perhaps explain the apparently too pronounced curvature of some of the curves.

However, an approach to the problem on the basis of kinetics does not seem to have been wholly without value. Although the final results may be re-

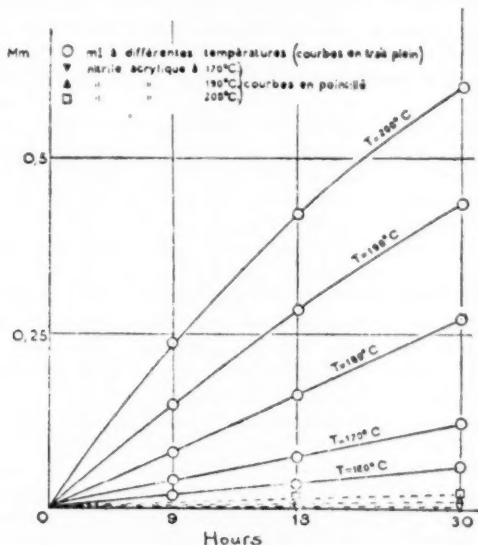


FIG. 7.—Quantities of maleic *N*-methylimide and acrylonitrile which combined with rubber in different times and at different temperatures. The Mm values (the quantities of each reagent) are calculated in gram-molecule per isoprene group.

- MI at different temperatures (solid curves)
- ▽ acrylonitrile at 170° C
- △ acrylonitrile at 190° C broken curves
- acrylonitrile at 200° C

garded as a failure, contributing little or nothing, they show once more the extreme complexity of the chemical reactions of natural rubber. Rubber is, in fact, a colloidal substance of biological origin, for which there are, from some viewpoints, no practicable methods of investigation.

THE RATE OF REACTION AS A FUNCTION OF THE TEMPERATURE

From the more practical viewpoint, it was interesting to know in what way the fixation of ethylenic compounds by rubber depends on the temperature. It has already been shown that a rise of temperature accelerates the reaction (see Figure 1).

In these experiments, maleic *N*-methylimide was again chosen, in addition to which acrylonitrile, $\text{H}_2\text{C}:\text{CHCN}$, also was tested. The latter was already known to react with rubber in the presence of a peroxide catalyst⁷. In all the experiments the same technique was used, *i.e.*, solutions in which the concentrations of rubber and of maleic *N*-methylimide or acrylonitrile were 0.4 gram-moles per liter (the concentration calculated at the temperature at which the reaction took place) were heated at several different temperatures.

The results are summarized in Table 1 and shown graphically in the curves of Figure 7, where *Mm* represents the quantity of ethylenic compound fixed per isoprene group of the rubber, and *R* represents the ratio of the values of maleic *N*-methylimide and acrylonitrile.

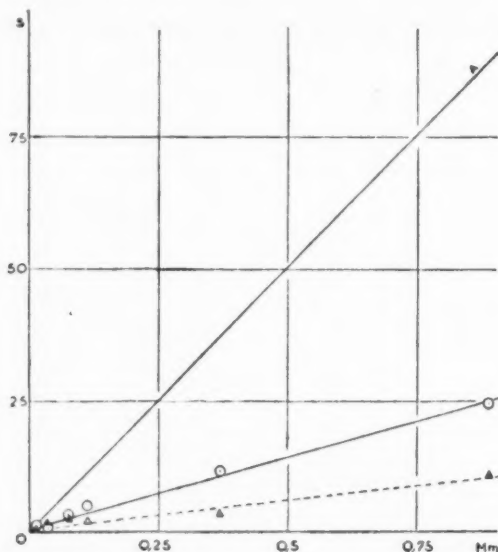


FIG. 8.—Increase of saturation (*S*) of rubber at 170° C as a function of the quantity of combined maleic *N*-methylimide (*Mm*). *Mm* is calculated in gram-moles per isoprene groups. *S* was determined by the iodine number (solid line) and by the bromine number (broken line).

Under the particular experimental conditions, acrylonitrile combines with the rubber at a rate 25 to 30 times as great as does maleic *n*-methylimide in the temperature range involved. These results show again that a rise of 10° C in the temperature approximately doubles the rate of fixation of maleic *N*-methylimide.

STUDY OF THE STRUCTURE OF THE REACTION PRODUCTS

With a view to explaining what becomes of the double bonds of the rubber when maleic *N*-methylimide is fixed, the unsaturation of some of the addition products which were prepared by the action of heat was measured. These determinations were made on products which had been obtained by heating, for 40 hours at 170° C, benzene solutions containing 0.4 gram-moles per liter or

rubber (b) and 0.03, 0.1, 0.2, 0.3, 0.4, 0.7, and 1 gram-mole per liter of maleic *N*-methylimide (a) (see the curves in Figure 5).

Determinations of the iodine numbers of these products proved that the losses of unsaturation (calculated with account being taken of the quantity of maleic *N*-methylimide fixed) were considerably less than those found previously when *p*-bromobenzoyl peroxide⁷ was used instead of a corresponding quantity of combined maleic *N*-methylimide. However, there was no certainty that the presence of maleic *N*-methylimide molecules on the rubber hydrocarbon chains did not set up some sort of an obstruction in these chains which prevented the complete fixation of iodine in the determination of unsaturation.

The idea then occurred that, by using bromine instead of iodine, since the bromine atom is smaller, this molecular obstruction would be less effective, though of course still present, and, therefore, lower unsaturation values might perhaps be obtained. Although this hypothesis is perhaps over-simplified, it is none the less true that the experimental results obtained seem clearly to confirm the hypothesis.

In view of this, the bromine number was determined by the method developed by Bloomfield⁸, which, according to him, does not involve any side reactions. An experimental comparison of the iodine number and bromine number (calculated as iodine) gave, for the original rubber, values of 357 and 358, respectively. These values are so nearly the same that there are evidently no more extensive substitution reactions in the one case than in the other.

The results are summarized in Figure 8, which shows the percentage reduction (*S*) of unsaturation of the rubber as a function of the number of gram-moles (*Mm*) of maleic *N*-methylimide fixed by one isoprene group. The curves showing *S* as a function of *Mm* are straight lines, the slopes of which are 0.27 and 0.12, respectively, depending on whether the *S* values were determined by the iodine or bromine values, when the slope of the straight line *OA* is by definition equal to 1. The straight line *OA* represents what would be the change of *S* if each molecule of combined maleic *N*-methylimide had resulted in the disappearance of one double bond of the rubber hydrocarbon. In other words, the reaction involves the disappearance of only a small part of the ethylenic bonds of the rubber, while the major part of the maleic *N*-methylimide becomes fixed at points other than these ethylenic bonds. It is, therefore, justifiable to assume that the small reduction of unsaturation is the result of secondary reactions (probably cyclization reactions) rather than of fixation of maleic *N*-methylimide.

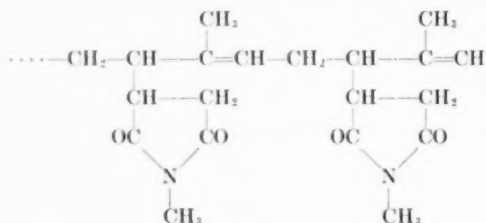
Thus one is led to the same conclusion as that reached in the case of the catalyzed reaction. Consequently it would seem that the structure of the addition compounds formed by the heat reaction likewise conforms with the views of Farmer, according to which the CH_2 groups of the rubber hydrocarbon chains located in α -position with respect to the double bond are capable of becoming dissociated under the influence of certain factors, with formation of free radicals:



The unsaturated derivative would then unite with the α -methylenic carbon atoms of the rubber, thereby losing its double bond and conserving the double bonds of the rubber.

It should be noted that, according to this scheme, fixation of more than one molecule of maleic *N*-methylimide per isoprene group is not possible, and this

conclusion was confirmed experimentally by the fact that in no case was even this proportion actually attained, even when a large excess of maleic *N*-methylimide was present and when the time of heating was prolonged.



It is reasonable to assume the existence of an analogous structure of the addition products of rubber and maleic anhydride and of rubber and acrylonitrile.

MECHANISM OF THE REACTIONS

Although this study of the kinetics of the reactions does not furnish any useful information on the mechanism of the reactions, at least a theory may be advanced which seems to conform to the facts.

It may be assumed that a chain reaction is involved, but there still remains a doubt of major concern, *viz.*, the nature of the initiation reaction. This may be attributed to various causes, such as:

(1) *The solvent itself.*—Cases are, in fact, known where the solvent can produce free radicals; for example, this is the basis of the hypothesis advanced by Naunton⁹ to explain the mechanism of photogelation.

(2) *Impurities present in the rubber.*—It is impossible to be sure that rubber, even where carefully purified, is absolutely free of all traces of peroxides.

(3) *Opening of the double bond of the ethylenic compound under the influence of heat, with liberation of a biradical.*—The existence of these double radicals has been accepted as a means of explaining the mechanism of the polymerization of styrene¹⁰.

If it is assumed, for the sake of simplification, that the reaction is initiated in accordance with this last process, and if the ethylenic compound is designated by E and the rubber by RH (H being the mobile hydrogen atom on α -methylene carbon atoms), then the following scheme is derived:

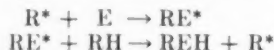
Formation of a biradical: $E \rightarrow *E*$

These biradicals are capable of forming free radicals on the rubber hydrocarbon chains by an initiation reaction:



The free radicals, $*EH$, can either unite with each other, with formation of dimers, or can initiate a second RH, with formation of HEH (corresponding to succinic *N*-methylimide in the case of maleic *N*-methylimide).

The free radicals, $R*$, then unite with the ethylenic compound, E, in accordance with a propagation reaction, in two steps:



and so forth, repeatedly. REH is the addition product, in the formation of which the ethylenic bond of the rubber hydrocarbon takes no part at any time.

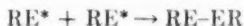
Finally, there are several possible termination reactions which would result in the formation of intermolecular bonds:



or



or



CHARACTER OF THE PRODUCTS OBTAINED

In the case of the reaction when catalyzed by a peroxide, insolubilization (gelation) occurs unless certain well defined conditions are adhered to; in particular there is this tendency when the concentration is higher than 3 per cent. In the case of the thermal reaction, this phenomenon was never observed up to concentrations of the order of 10 per cent. As mentioned, earlier the products are elastic or rubberlike masses when they contain relatively small proportions of combined ethylenic compound, are hard and brittle for relatively high proportions of combined ethylenic compound, and are white powders when more than 0.7 gram-mole of maleic *N*-methylimide per isoprene group of the rubber hydrocarbon has combined. These powders are soluble in cold acetone and in boiling alcohols.

CONCLUSIONS

In the first part of this work, it was pointed out that the aim of the investigation as a whole was to throw a little more light on the reaction, considered by itself, of rubber in solution with unsaturated compounds. It was hoped that it would be possible to apply the results obtained with maleic *N*-methylimide to acrylonitrile and thereby to obtain transformation products of rubber which would be resistant to solvents. But it was not found possible, at least on the basis of facts available at the time, to retain the elasticity of rubber in any vulcanizate and yet have a high enough content of combined acrylonitrile to furnish products resistant to solvents. It was, in fact, established that the development of a network structure associated with the decrease of elasticity is the result above all else of the vulcanizing effect of the peroxide. On the other hand, if a high percentage of acrylonitrile is to be fixed, the use of the peroxide is necessary, since the purely thermal reaction proceeds at a rate which is much too slow for any practical application.

Under these conditions, the simultaneous use of acrylonitrile and a peroxide would not seem to offer any solution of the problem, but even if acrylonitrile does not appear to be a satisfactory agent, this does not mean that there are not other unsaturated nitriles, the reactivity of which with rubber is comparable to that of maleic *N*-methylimide. If this is so, then it should be possible to carry out the reaction without a catalyst, whereby the principal cause of the development of a network structure would be diminished and the desired compromise of desired properties attained.

SUMMARY

The addition reaction at an elevated temperature (170° C) of maleic *N*-methylimide with natural rubber in solution was studied. Attempts were

made to apply the principles of kinetics to this thermal reaction with a view to understanding the nature of the reaction, but the complexity of the system made impossible any chance of attaining the results hoped for.

A comparison of the fixation of acrylonitrile and that of maleic *N*-methylimide in the temperature range of 160°–200° C showed that the rates of these two reactions are in the ratio of 1 to 25–30.

A determination of the unsaturation of the addition products showed that fixation is on the α -methylenic carbon atoms of the rubber hydrocarbon.

Finally a mechanism of the reaction is proposed, in which free radicals play a part.

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EFFECTS OF ANTIOXIDANTS ON RATE OF BREAKDOWN OF RUBBER DURING MASTICATION *

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INTRODUCTION

Piper and Scott¹ milled rubber with and without the addition of 2 per cent of hydroquinone on a cold mill. They could not detect any difference between the rates of breakdown. Wren made similar observations², but undefined experimental errors might vitiate his interpretation that phenols do not retard mastication. Phenyl- β -naphthylamine, however, has been reported³ to retard the breakdown of rubber during mastication in an internal mixer at 160° C. It was, therefore, decided to make an independent investigation.

PLASTICITIES

Plasticity measurements were made by a Williams plastometer: 2-gram samples of rubber, cut approximately spherical, were preheated 15 minutes at 70° C, followed by three minutes compression in the plastometer under 5-kg. load at 70° C. Cigarette paper was used to prevent the pellets sticking to the plastometer plates. The results are recorded as height of pellet in 0.01 mm.

EFFECT ON MILLING

The procedure was to masticate 200-gram lots of pale crepe rubber on a 9-inch mill, with the rolls running at a friction ratio of 2:1. The nip width was kept constant throughout each series of experiments. A bank was formed as soon as possible, and the thin rubber sheet was not cut except to obtain samples for plasticity determinations. These samples were taken from one edge of the sheet of rubber on the roll. The antioxidants were added early and uniformly. With the largest amounts used this took 1.5 minutes.

Phenolic compounds reduce the rate of oxidation of olefins by combining with the peroxide radical chain carriers⁴. The antioxidants chosen were pyrogallol and hydroquinone.

In the first experiments the mill rolls were water cooled and were at 20° C when the rubber was added. The results are given in Table 1. From the experimental error as shown by the repeat experiment it is obvious that no differences in the rate of breakdown are indicated.

* Reprinted from the *India-Rubber Journal*, Vol. 120, No. 21, pages 825-826, May 26, 1951.

TABLE 1
EFFECT OF ANTIOXIDANTS DURING COLD MILLING

Pyrogallol added (%)	Plasticity	
	5 min. masti- cation	10 min. masti- cation
0	427	309
0	431	295
0.25	437	300
1.0	446	278
2.5	435	281
5.0	431	300

The experiments were repeated with the roll temperatures initially $100 \pm 2^\circ$ C. At the end of ten minutes' mastication, both rolls were 2 to 3° C hotter. The results obtained are given in Table 2.

The results with a peptizing agent, Vulcamel (a technical product of the aromatic mercaptan type), showed that the method used would detect peptizing action, but the results with pyrogallol and hydroquinone did not indicate

TABLE 2
EFFECT OF ANTIOXIDANTS DURING HOT MILLING

Percentage added	Substance added	Plasticity	
		5 min. masti- cation	10 min. masti- cation
0	—	515	454
0	—	535	473
0.5	Pyrogallol	580	469
1.0	Pyrogallol	529	470
2.0	Pyrogallol	555	486
0.5	Hydroquinone	520	450
1.0	Hydroquinone	514	453
2.0	Hydroquinone	526	456
0.5	Vulcamel	457	388

any retarding action. It was, however, thought significant that the plasticities given by the rubbers to which pyrogallol had been added were higher than those developed under the influence of hydroquinone, although still within the limits of experimental error.

Pyrogallol is twelve times more effective as an antioxidant during the autoxidation of squalene than is hydroquinone⁵. Therefore these results might

TABLE 3
EFFECT OF ANTIOXIDANTS DURING HOT MILLING (REPEAT)

Percentage added	Substance added	Plasticity	
		5 min. masti- cation	10 min. masti- cation
0	—	527	476
0	—	533	458
0.5	Pyrogallol	540	472
1.0	Pyrogallol	531	455
2.0	Pyrogallol	546	472
0.5	Hydroquinone	531	484
1.0	Hydroquinone	532	460
2.0	Hydroquinone	544	479

indicate a slight retarding effect by the pyrogallol. The experiments were accordingly repeated, and the results are given in Table 3.

These results do not confirm the suspected influence of pyrogallol; so it must be concluded that antioxidants do not affect the softening of rubber during milling, or that any such effect is too slight to be detected because of the variability of repeated determinations.

EFFECT ON HIGH TEMPERATURE MASTICATION

Lots of 1000 grams of pale crepe rubber were masticated in a small Banbury internal mixer at high temperature. The antioxidants were added after 0.5 minute of mastication. The temperatures of the rubbers immediately on discharge from the mixer were 166–167° C. Hydroquinone sublimed on to the floating weight in the mixer and was not used.

TABLE 4
EFFECT OF ANTIOXIDANTS DURING HOT MASTICATION

Substance added	Amount added (%)	Time of mastication (min.)	Plasticity
—	—	7.5	297
Pyrogallol	2	7.5	371
Phenyl- β -naphthylamine	2	7.5	320
—	—	7.5	300
—	—	10	246
Phenyl- β -naphthylamine	2	10	284
Pyrogallol	2	10	341
—	—	10	229

The results are given in Table 4 in the order in which the samples were masticated. Both antioxidants retard the rate of breakdown at high temperature.

EFFECT ON LOW TEMPERATURE MASTICATION

At 77° C phenyl- β -naphthylamine does not retard the rate of breakdown of rubber in an internal mixer³. Pyrogallol has a greater effect than phenyl- β -naphthylamine at high temperatures, so it was decided to investigate the effect of the former at a lower temperature.

TABLE 5
EFFECT OF PYROGALLOL ON LOW TEMPERATURE MASTICATION

Percentage added	Plasticity (10 min. mastication)
0	413
2	421
0	407
2	410

Lots of 1000 grams of pale crepe rubber, with or without pyrogallol, were masticated in the small water cooled internal mixer, in the order given in Table 5. The temperatures of the rubbers at the end of each mastication were 80 to 84° C.

It is apparent that pyrogallol has no effect on the rate of breakdown during low temperature mastication.

DISCUSSION

Certain observations⁶ can be interpreted that the mechanism of mastication at cool mill temperatures may be essentially the same as that of ordinary thermal autoxidation of raw rubber. The former autoxidation occurs more rapidly than the latter, indicating that mastication induces large numbers of free radicals. Available oxygen can then readily react with rubber, irrespective of whether some reaction chains are terminated by antioxidant activity. Chain stoppers do not, therefore, affect the rate of breakdown of rubber during low temperature mastication.

ACKNOWLEDGMENTS

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AUTORADIOGRAPHIC TECHNIQUE WITH CARBON¹⁴ IN RUBBER *

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In the manufacture of rubber products such as tire treads, additives such as carbon black and zinc oxide are incorporated into the rubber to give special desirable characteristics. These additives are dispersed by mixing or milling, and it is important that they be well dispersed throughout the rubber. The uniformity of dispersion of carbon black in rubber is generally reflected by the stress-strain properties of the loaded rubber stocks. But low modulus, elongation, or tensile strength values are also caused by polymer breakdown. The method used by the authors to study the distribution of carbon black in rubber was a visual observation of the carbon black dispersed in the rubber, made possible by the autoradiographic technique with carbon¹⁴.

Carbon¹⁴ is an isotope of carbon and is chemically the same as the carbon atoms in the carbon black; the only difference is that it has a higher atomic weight and is radioactive, emitting soft beta particles having an upper energy limit of only 150 to 170 kv.

Autoradiography is a technique by which radioactivity present in a material can be precisely located. This technique utilizes Becquerel's discovery that radioactivity affects photographic emulsions, producing a blackening of the film. The first autoradiographs using carbon¹⁴ were obtained by Grosse and Snyder¹. Making use of this technique, a trace of radioactive carbon (carbon¹⁴) was incorporated into the carbon black to be used, and the radioactive carbon black was then dispersed into the rubber. Samples of cured and uncured rubber containing the radioactive carbon black were put into direct contact with x-ray film, and after a suitable exposure time the films were developed. The radiations given off by the radioactive carbon blackened the films, producing patterns which are pictures of the carbon black as distributed in the rubber.

In order to make an autoradiograph, sufficient radioactivity must be present in the material being studied; otherwise long exposure times are required. A total flux of $\cong 10^5$ beta particles per square centimeter of film is necessary to produce a detectable blackening, and at least 10 to 100 times this activity is needed to produce a satisfactory image².

EXPERIMENTAL PROCEDURE

Selection of method for introducing carbon¹⁴ into carbon black.—Before any work could be done, the carbon black (Philblack-O) had to be made radioactive without increasing its particle size. The radioactive carbon (carbon¹⁴) was introduced into the carbon black by four different methods. Samples of the radioactive carbon black from each of the four methods were taken, and the

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TABLE I
PARTICLE SIZE OF RADIOACTIVE PHILBLACK-O

Method of preparing radioactive Philblack-O	Numerical average particle size, A
Regular Philblack-O	350
Impregnation of Philblack-O with sodium acetate containing carbon ¹⁴	296
Impregnation of Philblack-O with glycine containing carbon ¹⁴	314
Decomposition of glycine containing carbon 14 on Philblack-O	302
Reaction of Philblack-O with carbon dioxide containing carbon ¹⁴	290

particle size was determined by means of the electron microscope. A comparison of their particle sizes, including regular Philblack-O, is shown in Table I. None of the four methods of preparing radioactive carbon black significantly affects the particle size of the black. While preparing these samples, it was seen that the radioactive carbon black was best and most economically prepared by reacting at elevated temperatures with radioactive carbon dioxide ($C^{14}O_2$).

Preparation of radioactive Philblack-O from $C^{14}O_2$.—The apparatus used to prepare the radioactive carbon black is shown in Figure 1.

Twenty-five grams of Philblack-O was put into a quartz tube, 3, and degassed by heating at $1000^\circ C$ for 3 hours and pumping off all the adsorbed gases. Then 35 mg. (0.5 millicurie) of radioactive barium carbonate ($BaC^{14}O_3$) was put into the decomposition tube, A, and decomposed in vacuo by adding dropwise 6 cc. of 40% phosphoric acid. The liberated radioactive carbon dioxide ($C^{14}O_2$) was first passed through dry ice trap, 1, to remove water, and was finally condensed in liquid nitrogen trap 2. The radioactive carbon dioxide was then distilled into the quartz tube, 3, containing the degassed Philblack-O.

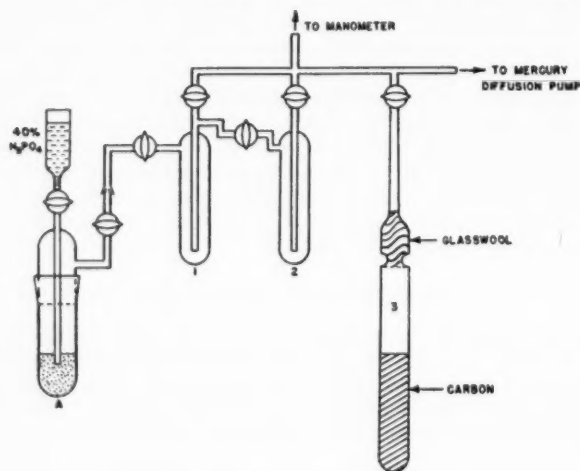
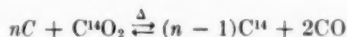


FIG. 1.—Apparatus for preparing radioactive carbon.

The radioactive carbon dioxide and the Philblack-O were heated for 5.5 hours at 900° to 1000° C.



As a very large quantity of carbon black (25 grams) was used compared to the amount of carbon (2.2 mg.) in the radioactive carbon dioxide, the carbon monoxide formed and carbon dioxide present had only infinitesimal amounts of radioactivity; the radioactivity was in the carbon black. The carbon monoxide and carbon dioxide were pumped off the radioactive Philblack-O, and the radioactive black was ground and well mixed.

A sample (greater than 30 mg. per sq. cm.) of the radioactive black gave 22,500 counts per minute when put into a dish 2.5 cm. in diameter and measured with Technical Associates thin mica window Geiger counter (3.8 mg. per sq. cm. thick). This is equivalent to 0.5 millicurie of carbon¹⁴ per 25 grams of carbon black. The 25 grams of radioactive Philblack-O were diluted with 236 grams of regular Philblack-O by repeated stirring, spreading, and quartering to give 261 grams of diluted radioactive carbon black. A dish 2.5 cm. in diameter, containing a sample (>30 mg. per sq. cm.) of the diluted radioactive

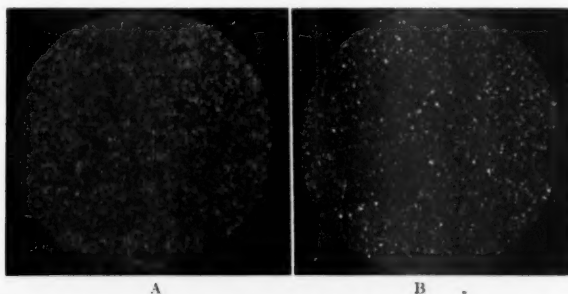


FIG. 2.—Autoradiographs of radioactive Philblack-O. Kodak No-Screen x-ray film. A—Concentrated, 1-hour exposure, 100 μ c. per gram of carbon. B—Diluted, 45-hour exposure, 2 μ c. per gram of carbon.

carbon black, gave 2700 counts per minute (= 0.5 millicurie of C¹⁴ per 261 grams of carbon black) on the Geiger counter, thus showing good mixing.

The concentrated and diluted radioactive carbon blacks were exposed to Kodak No-Screen x-ray film.

The autoradiographs obtained after 1- and 45-hour exposures (Figure 2) show how well the carbon black was mixed.

General technique and film.—To obtain a clear autoradiograph, close direct contact is necessary between the emulsion of the film and the material being studied. Recently photographic printing frames have been used with excellent results³. These frames apply a gentle and even pressure, thus obtaining uniform contact between film and sample.

Throughout the work reported, the photographic printing frame, with the glass plate replaced by brass, was used as the camera for obtaining autoradiographs. For the radioactive rubber samples a sheet of film was inserted into the camera (printing frame) and the sample was placed on top of the film, thus making direct contact with the film. When radioactive carbon black samples were to be autoradiographed, a rubber sheet containing several holes 1 inch in

TABLE II
COMPOSITION OF RUBBER MIXES

Substance	Weight (grams)
Zinc oxide	19.6
Philblack-A	65.1
Philblack-O (radioactive)	261.0
Stearic acid	13.1
Antioxidant 1	4.0
Antioxidant 2	2.6
Plasticizer 1	27.7
Plasticizer 2	37.5
Sulfur-rubber mix	57.2
Rubber polymer ^a	606.0
Accelerator	6.2
Total 1100.0	

^a 41° F low-temperature polymer was used in this work. This technique is equally valid for any polymer.

diameter was placed on top of the film. These holes were half filled with the radioactive carbon black and covered with rubber plugs. When the camera was closed, the rubber plugs pressed the black against the film, giving close direct contact. After a sufficient exposure^a time, the film was removed and developed with the proper developer.

Previous experimenters⁴ have found that emulsions intended for the registration of x-rays will, in general, produce the most rapid response to beta radiations. X-ray film owes its sensitivity to very large grain size, and to the presence of an emulsion coating on both sides of backing.

The films⁴ most commonly used for beta-ray autoradiographs are the Kodak No-Screen, Ansco No-Screen, and Ansco Superay-A x-ray films⁵.

In order to determine which films were best for the authors' work, autoradiographs were obtained of the concentrated radioactive Philblack-O, using each of the three x-ray films. Kodak No-Screen and Ansco No-Screen were the faster films (more sensitive). The Ansco Superay-A film had much better resolution than the No-Screen films, but was less sensitive and required about

TABLE III
PHYSICAL PROPERTIES OF RADIOACTIVE CARBON-RUBBER MIXES^a

Mix	Tensile strength (lb./sq. inch)	Elongation (%)
A	375	110
B	725	205
C	1100	315
D	1500	390
E	1800	420
F	3200	515
L	2225	450
M	2575	530
N	2800	590
O	2875	520
P	3125	590
Q	3350	620
R	3225	600

^a All data are average of two tests.

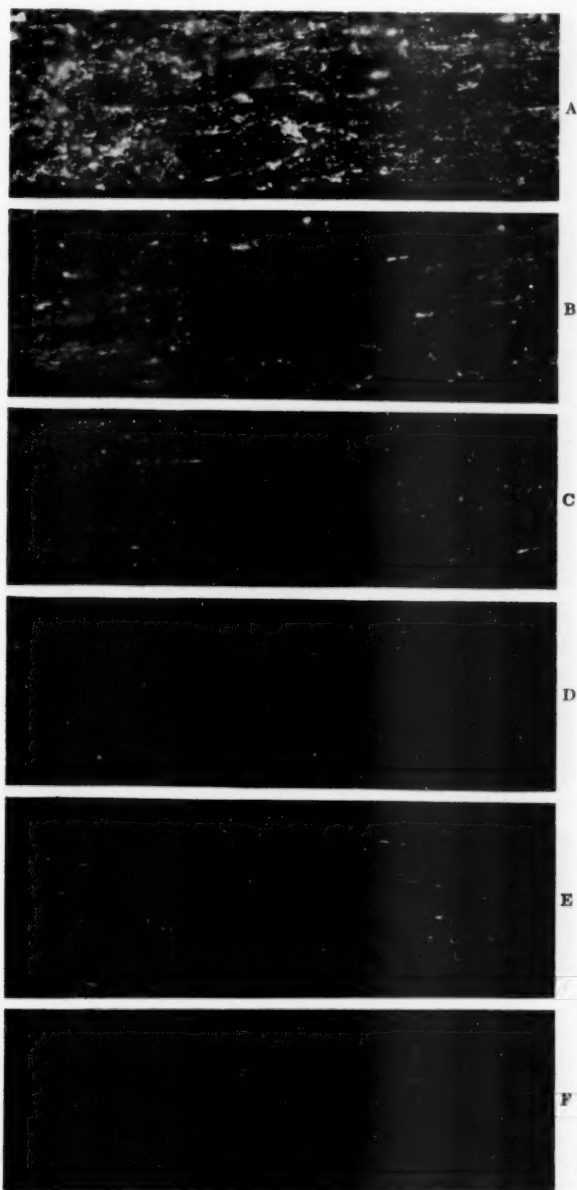


FIG. 3.—Unneured rubber strips containing carbon¹⁴. Direct contact, 71.5-hour exposure, Ansco No-Screen x-ray film mixes A to F.

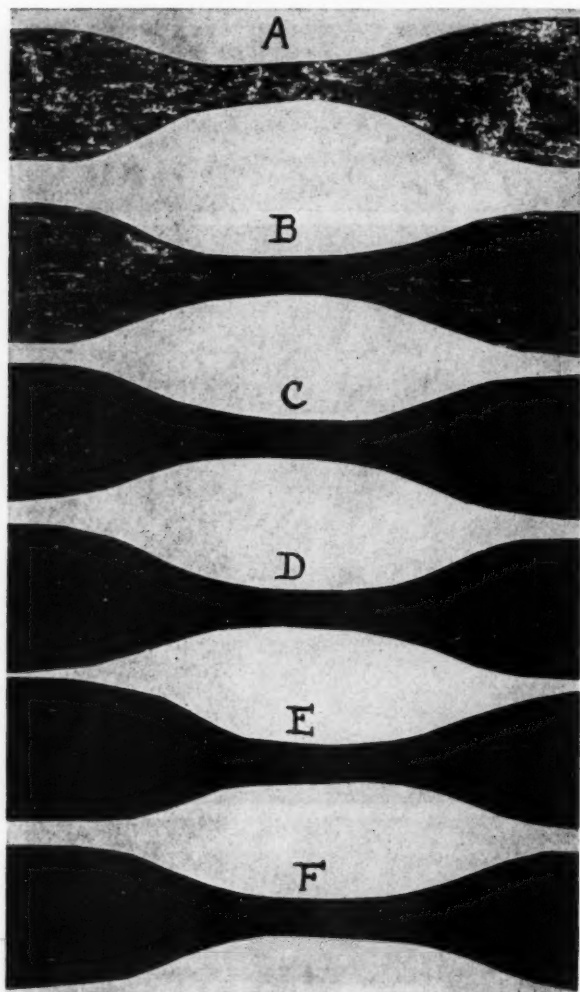


Fig. 4.—Vulcanized strips used for tensile strength containing carbon¹⁴. Direct contact, 58-hour exposure, Ansco No-Screen x-ray film mixes A to F.

four times the exposure time of the No-Screen films. Therefore, in order to get a good picture in a reasonable length of time, either the Kodak or Ansco No-Screen x-ray film should be used with the radioactive rubber samples. Ansco No-Screen x-ray film is developed with Liquidol and fixed with Liquifix; Kodak No-Screen x-ray film makes use of either Kodalk or Kodak D-19 as the developer and Kodak x-ray fixer as the fixer.

Preparation and physical properties of rubber mixes containing radioactive carbon.—The compositions of the 41° F low-temperature polymer mixes con-

taining radioactive carbon black used throughout this work are shown in Table II.

In order to see whether the autoradiographic technique can differentiate between good and poorly dispersed carbon black-rubber mixes, good and poorly dispersed mixes were made on both the laboratory-sized Banbury and the roll mill.

Mix A, which represented the most poorly dispersed stock, was given a 3-minute mix in the Banbury, followed by three passes through the roll mill

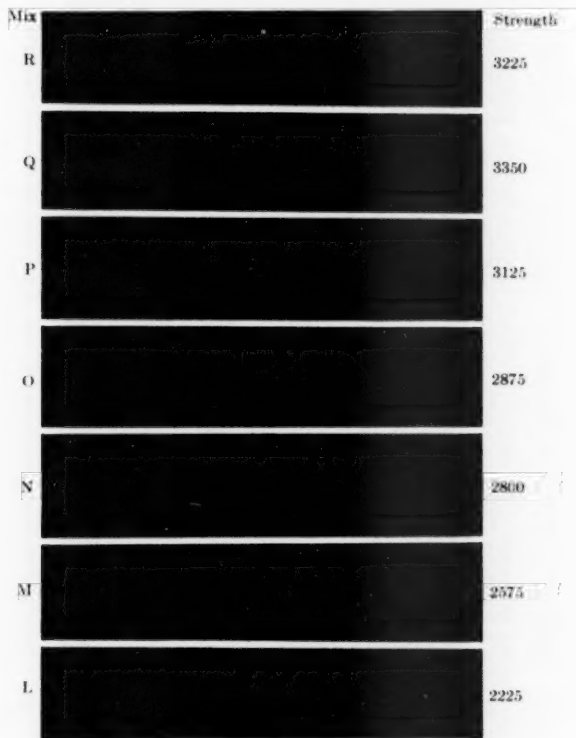


Fig. 5.—Vulcanized rubber strips containing carbon¹⁴. Direct contact, 72-hour exposure, Ansco No-Screen x-ray film mixes L to R.

without banding. The dispersion of the carbon black was progressively improved for mixes B to E by additional passes through the mill. Mix F was prepared on the Banbury using the two-cycle procedure (a 6.5-minute first cycle followed by a 2-minute second cycle) followed by three passes through the roll mill with banding.

Mix L was prepared like mix A, but had a 4-minute instead of a 3-minute mix in the Banbury. The dispersion of the carbon black in mixes M to R was progressively improved by additional passes through the mill.

The physical properties of the mixes are shown in Table III.

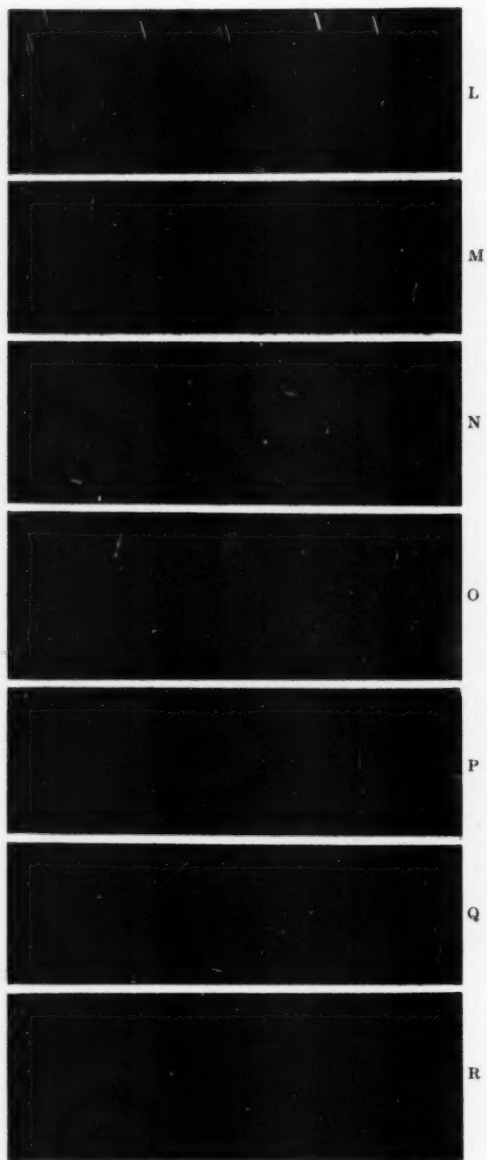


FIG. 6.—Uncured rubber strips containing carbon¹⁴. 72-hour exposure, Anasco No-Screen x-ray film mixes L to R

[*Autoradiographs of rubber containing carbon¹⁴.*—Autoradiographs were made of cured and uncured samples of the different mixes by exposing the radioactive rubber samples to Ansco No-Screen x-ray film for about 3 days (68 to 72 hours). The exposed films were then developed with Liquidol for 4 minutes at 68° F and fixed with Liquifix. Figure 3 shows the autoradiographic pictures of uncured samples of mixes A to F; Figure 4 shows the same for the cured samples.

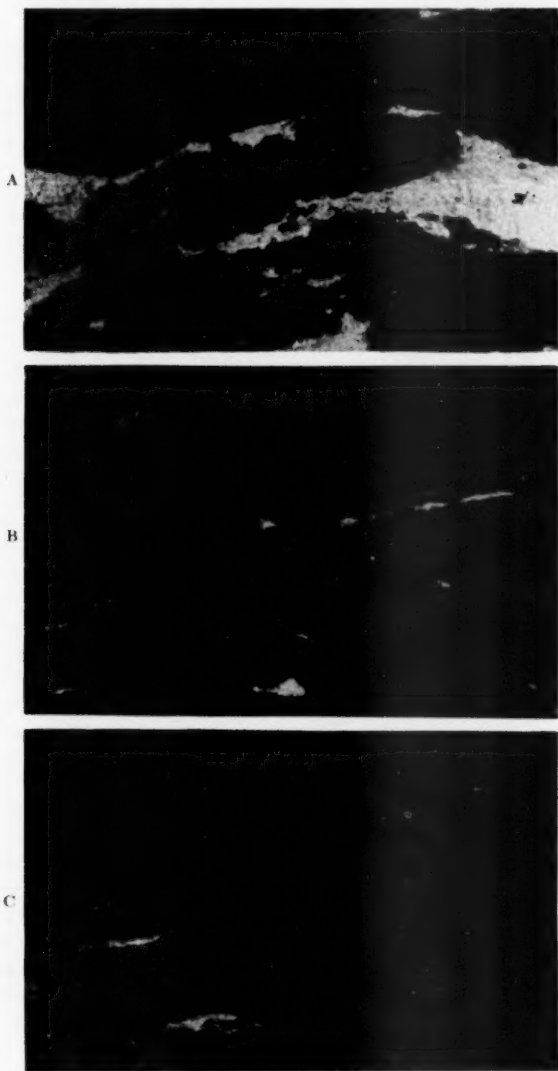


FIG. 7.—Photomicrographs of vulcanized samples of mixes A to F, $\times 20$. 10- μ sections.

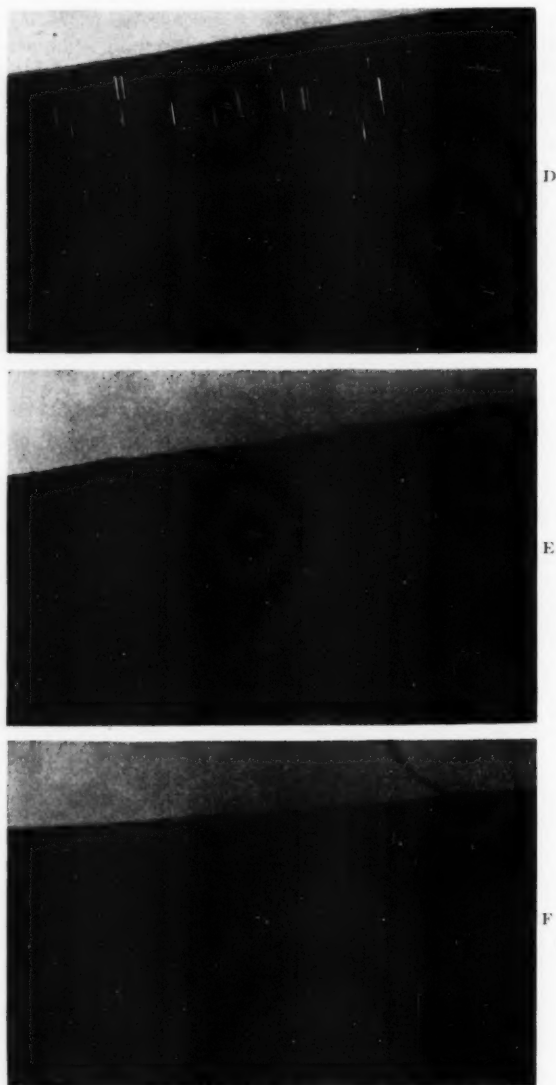


FIG 7.—Continued

The autoradiographs of cured and uncured samples of mixes L to R are shown in Figures 5 and 6, respectively.

DISCUSSION OF RESULTS

An examination of the autoradiographs in Figures 3 to 6 shows that the pictures of the different mixes correlate nicely with the physical properties of

these mixes—that is, as the tensile strength increases, the dispersion of the carbon black in the rubber becomes more uniform. This holds until a tensile strength of 2800 to 2900 pounds per square inch is obtained for this rubber formulation. The autoradiographs of mixes having this tensile show the carbon black to be uniformly dispersed. No increase in carbon black dispersion can be observed in the autoradiographs of mixes having tensile strengths greater than 2800 to 2900 pounds per square inch.

A study of Figure 3 shows that in the poor mixes the images indicate in which direction the rubber flowed through the mill.

Photomicrographs were made of 10 μ sections of mixes A to F prepared by microtome sectioning (Figure 7). A comparison of these photomicrographs with the autoradiographs of mixes A to F shows that the autoradiographic technique is much superior to the photomicrographic technique in studying carbon dispersion in rubber; the photomicrographs show no differences between mixes D, E, and F.

A great deal of detail showing the differences between the various mixes is lost in the photographs of Figures 3 to 7 that are observed in the original pictures.

APPLICATION OF AUTORADIOGRAPHIC TECHNIQUE IN RUBBER

The autoradiographic technique can be useful to the rubber industry in numerous ways. It can be used to study the dispersion of carbon black or any other component of the rubber mixture, to determine the causes of carbon black agglomeration in rubber, to study the surface contour of rubber, etc.

An example of the use of the autoradiographic technique in studying the causes of carbon black agglomeration in rubber is shown in the following experiment.

Some uncured and unaged rubber containing carbon¹⁴ (mix E) was aged with and without air circulation for 4 days at 70° C. Autoradiographs were obtained of the unaged rubber, the rubber aged with air circulation, and the rubber aged without air circulation. The autoradiograph obtained for the unaged rubber showed that the particles of carbon black were dispersed at random. A comparison of the autoradiographs obtained from the aged rubber showed that only a little agglomeration and alignment of the carbon black took place when the rubber was aged with air circulation; the sample aged with no air circulation had a great deal more carbon black agglomeration and alignment. The same results were obtained when the samples were first cured and then aged.

SUMMARY

The autoradiograph technique making use of carbon¹⁴ is useful in studying the carbon black distribution in rubber.

It is superior to the photomicrographic technique in studying carbon black dispersion in rubber. Autoradiographs of different carbon black-rubber mixes (tensile strengths varying from 300 to 3300 pounds per square inch) showed visible variations in the carbon black distribution which closely agree with the tensile strength data, whereas photomicrographs of the same mixes showed no differences among the various mixes.

The autoradiographic technique is also useful in tracking down carbon black agglomeration in rubber.

ACKNOWLEDGMENT

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THE HEAT SENSITIVITY OF HEVEA LATEX

I. THE ACTION OF ZINC-AMMONIUM COMPLEXES *

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INTRODUCTION

Several processes in current use for the heat sensitization of latex are based on the more or less direct action of zinc-ammonium complexes.

The use of ammonium nitrate in the Kay process has spread into many countries, and it doubtless is the most effective inorganic salt. When salts of weaker acids such as ammonium carbonate are employed, the sensitizing action is considerably less. The explanation of this phenomenon seems then to lie in the high strength of the acid which is a component part of the complex. However, when following the procedure of adding a solution of a zinc-ammonium complex, prepared beforehand, to latex, we observed that zinc ammonium acetate had a greater heat-sensitizing effect than did zinc ammonium sulfate. But acetic acid, is a weak acid; its ionic strength cannot, therefore, be involved in this case.

It was necessary to explain this anomaly, and, from a more practical viewpoint, to see if there were not some other complex salts of weak acids which could function as new sensitizing agents. With this in view we studied the formation of the zinc ammonium complexes by determining the quantities of zinc solubilized during this formation.

FORMATION OF ZINC AMMONIUM COMPLEXES

The role of zinc oxide in the heat sensitization of latex has often been utilized, without, however, considering its true solubility, and with no regard to the type of the zinc oxide used. For this reason we first prepared pure zinc oxide by oxidation in air of zinc oxide distilled in bead form, and measured the solubility of this oxide in pure water and in the ammoniacal solutions by the so-called "color sensitive" method, based on the characteristic coloration imparted by dithizone (diphenylthiocarbazone).

SOLUBILIZATION OF ZINC OXIDE

The solubility of pure zinc oxide in pure water has been known for a long time, but not all the values given in the literature agree. We ourselves found

TABLE I
SOLUBILITY OF COMMERCIAL ZINC OXIDES IN 1-NORMAL AMMONIA

Pure zinc oxide	0.32 gram per liter
Commercial zinc oxide No. 1	1.17 gram per liter
Commercial zinc oxide No. 2	0.65 gram per liter

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Revue Générale du Caoutchouc*, Vol. 28, No. 1, pages 39-42, January 1951, and No. 2, pages 105-107, February 1951.

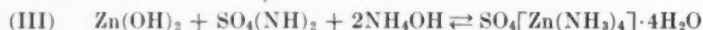
a solubility of 1 mg. per liter at 20° C, a very low value, but a value which increases rather rapidly if increasing quantities of pure ammonia in pure water are added. Even then the solubility is still only 0.32 g. per liter in 1-normal ammonia; it is greater if commercial products are used (see Table I).

But the solubility increases if an ammonium salt is also present; for example, in the presence of ammonium sulfate in normal solution and of ammonia in normal solution, this solubility is as high as 5 grams per liter.

This greater solubility is the result of the formation of a complex salt according to the reaction (I):



In order to verify the correctness of this reaction and to avoid the influence of the particle size of the zinc oxide on the rate of its solubilization, we used a zinc sulfate solution to which we added determined quantities of ammonia, and obtained the following results.



FORMATION OF THE ZINC AMMONIUM SULFATE COMPLEX

Starting with a known quantity of zinc sulfate in a solution of known normality, and by measuring polarographically the quantity of soluble zinc after each addition of ammonia of known normality, we found:

(1) that reaction (II) actually takes place, regardless of the concentration of zinc salt or ammonia.

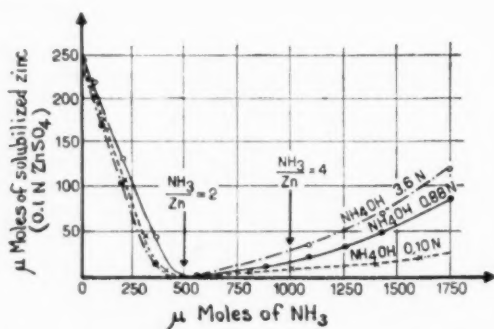


Fig. 1.—Influence of the concentration of ammonia on the formation of the zinc-ammonium complex compound.

(2) the reaction (III) proceeds to completion only at high concentrations.

At low concentrations, a hydrolytic phenomenon is observed which could cause the formation of an undissociated base, $\text{Zn}(\text{NH}_3)_4(\text{OH})_2$, reported by de Wijs². Therefore in dilute solution, only a small amount of complex can form. But then what is the behavior of a complex salt which is formed from a weak acid, as is the case with ammonium zinc acetate?

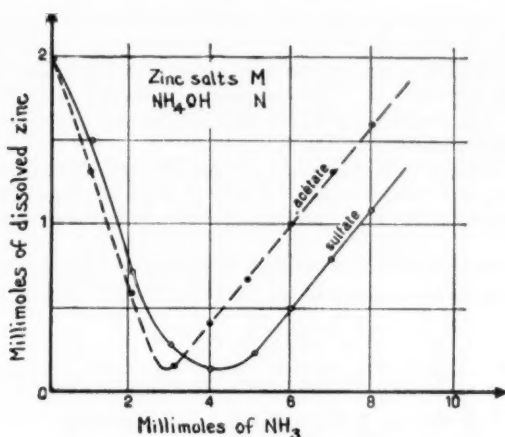


Fig. 2.—Difference between the capacity of the acetate and that of the sulfate to form complex zinc-ammonium salts.

FORMATION OF COMPLEX OF ZINC AMMONIUM ACETATE

Starting with a molar solution of zinc acetate, if increasing quantities of 1-normal ammonia are added and the zinc remaining in solution is determined after each addition, we find:

(1) That zinc acetate, easily hydrolyzable, precipitates more rapidly in the presence of ammonia than does zinc sulfate. Maximum precipitation takes place in the case of the acetate, with the ratio, NH_3/Zn about 1.5, which invalidates the theoretical equation III.

(2) The precipitate then dissolves more rapidly and, consequently, the formation of the zinc ammonium acetate complex is more rapid and more nearly complete.

Thus, with a much smaller quantity of ammonia, we obtain, if we start with zinc acetate, a much larger quantity of the complex than if we start with zinc sulfate (see Figure 2).

COMPARISON OF SOME INORGANIC COMPLEXES

We find that the ease with which a zinc salt passes into the state of a zinc-ammonium complex is related to the quantity of ammonia necessary to form

TABLE II
RELATION BETWEEN THE CAPACITY OF A SALT TO FORM A
COMPLEX AND ITS HEAT-COAGULATING POWER

Molar zinc salts (2 cc.)	Volume of N NH_4OH added to redissolve $\text{Zn}(\text{OH})_2$ (cc.)	Coagulation time at 50° C (minutes)
Formate	11	2½
Acetate	12	3
Nitrate	14	3½
Chloride	16	4½
Sulfate	25	6½
Carbonate	25	30

this complex. It should be noted also that this quantity of ammonia is in turn related to the heat-coagulating power of the complex (see Table II)

The heat coagulating power has been measured when hot according to a method described by Lepetit³. This property corresponds to the time necessary for 5 grams of latex containing 60 per cent dry rubber and 0.5 cc. of a molar solution of complex salt to coagulate at 50° C.

If instead of adding a definite volume of complex salt in molar concentration, there is added in each case an equal quantity of complex, based on the NH_3/Zn ratios, one obtains for each of these ratios a specific heat coagulating power of the complex.

The curves in Figure 3 show clearly the difference between the acetate and the sulfate, although the amount of complex concerned is exactly the same.

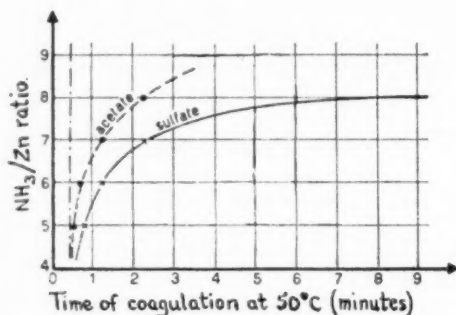


FIG. 3.—Specific heat-coagulating power of complexes introduced in equal amounts, based on the NH_3/Zn ratios.

As a result, the heat coagulating power of a complex zinc ammonium salt does not depend solely on the concentration of the $\text{Zn}(\text{NH}_3)_4$ cation, but depends also on the nature of the anion, which acts more or less directly on the hydrolysis of the zinc salt in solution, on the state of ionization of the complex, etc.

ACTIVITY OF ZINC-AMMONIUM COMPLEXES

We have seen that certain weak acids (formic acid and acetic acid) can form zinc-ammonium complexes, the heat coagulating power of which is rather high, whereas other weak acids (carbonic acid) are practically incapable of forming such complexes, unless the latex has been degraded⁴. It was then necessary to compare the heat coagulating activity of a large number of complexes formed from organic acids.

THE ACTIVITY OF COMPLEXES FORMED FROM FATTY ACIDS

The activity of complexes differs greatly according to the lengths of their chains and the degree of unsaturation of the fatty acid involved. Table III shows that, for a given concentration, *i.e.*, a normal solution of the complex salt, the activity of the complexes ranges from 1 to 40.

Influence of the chain length.—The heat sensitivity is very evident for the first members of the aliphatic series (from formic acid to caproic acid), but decreases in proportion to the increase of the molecular weight and becomes very slight in the case of stearic acid.

The diacids like malonic acid, succinic acid, and adipic acid do not form active complexes. In a general sense it may be said that diacids are less effective than are monoacids with the same number of carbon atoms in the chain. Alcohol acids and cyclic acids have only a slight heat sensitizing action.

Influence of the double bond.—Only unsaturated fat acids seem capable of giving active compounds. Thus the compound formed from undecylenic acid is 15 times as active as the compound formed from undecylic acid; it is the same with zinc ammonium oleate in comparison with zinc stearate.

What about fatty acids? We know that the presence of a double bond, especially in a fatty acid, profoundly changes its surface-active properties. It becomes possible to obtain a more extended film in a liquid-air interface and to decrease the expansion temperature.

TABLE III
THERMOCOAGULATING POWER OF COMPLEXES FORMED FROM
DIFFERENT ORGANIC ACIDS

			Time of coagulation at 70° C
Saturated acids	Monoacids	formate	12 minutes
		acetate	12 minutes
		butyrate	12 minutes
		valerate	13 minutes
		caproate	15 minutes
		oenanthylate	22 minutes
		caprylate	40 minutes
		undecylate	50 minutes
		palmitate	>1 hour
		stearate	>1 hour
	Diacids	malonate	>1 hour
		succinate	>1 hour
	Alcohol acids	adipate	40 minutes
		malate	50 minutes
Unsaturated acids	Monoacids	tartrate	50 minutes
		undecylenate	3 minutes
	Diacid Cyclic acid	oleate	14 minutes
		fumarate	40 minutes
		benzoate	>1 hour
Amino acids	Monoacid series	—	>2 hours
	Diacid series	—	15' to 25 minutes

A series of chains of zinc ammonium oleate in latex show a certain mutual attraction, with the formation of micelles; this phenomenon likewise is observed in the case of a complex stearate. In the case of the oleate, however, these micelles have a stronger attraction for water, which may in part explain the marked thickening which is observed when latex containing a complex oleate is heated. It might then be assumed that since the volume of free water decreases, the rubber particles, by the effect of the Brownian movement, although hindered by the viscosity of the medium, would have a much better opportunity, on the one hand, to absorb the positively charged complex ions, and, on the other hand, to come in contact with one another more easily and thus to induce coagulation.

If we accept this theory, we can predict that the fatty acids which carry an α, β -double bond with respect to the carboxyl group would have greater heat coagulating power than fatty acids bearing a double bond in the middle of the

chain, since the expansion temperature of the former, in a liquid-air interface, is much less than that of the latter. Thus the complex undecylenate is much more active than the complex oleate.

ACTIVITY OF COMPLEXES FORMED FROM AMINO ACIDS

Because of the presence of amino acids in latex serum, and in particular in the serum of degraded latex, it is likewise interesting to find out whether these amino acids can form complex dissociable compounds under hot conditions and thus acquire a certain heat-coagulating power.

The zinc salts of amino acids are readily obtained by the action of amino acid on a dispersion of zinc oxide. Some of these salts are crystallizable, such as zinc glycolate; some are oily when hot, such as zinc aspartate.

Monocarboxylic amino acids.—If normal ammonia is added to a molar solution of zinc glycolate, no turbidity is observed⁵. On the contrary, if sodium hydroxide is added to the same solution, the product immediately becomes turbid as a result of the formation of zinc hydroxide. Thus glyecol is incapable of combining with ammonia, and consequently, its zinc salt can not form an ammonium complex. This is true also of all the other monocarboxylic amino acids. We must then beware of concluding, as some authors have already done, that all amino acids form ammonium salts with ammonia.

Dicarboxylic amino acids.—The amino diacids such as aspartic and glutamic acids give a precipitate of zinc hydroxide when ammonia is added to their zinc salts, but in this case the quantity of ammonia necessary to redissolve the precipitate is equal to one-half the calculated quantity.

Accordingly only one acid function reacts. In the case of monoacids, the proximity of the amino and carboxyl groups paralyzes the strength of the latter, which then acts only as a very weak acid. However, if the acid function is blocked with formaldehyde, zinc salts can be obtained from amino monoacids. These salts are resinous; are soluble in water, and can heat-sensitize latex.

Heat coagulating power of amino acids.—The heat coagulating power of these amino acids on an ammoniated latex in the presence of zinc oxide corroborates the previous results and can be summarized thus:

- (1) monocarboxylic amino acids: no power.
- (2) dicarboxylic amino acids: appreciable heat coagulating power (see Table III).

CONCLUSIONS

Among the different processes for heat-sensitizing latex by the more or less direct action of zinc-ammonium complexes, one has the choice of inorganic and organic complexes.

Among the inorganic complexes, zinc-ammonium nitrate seems to be the most effective. Prepared from a 5 *N* solution of zinc nitrate and 5 *N* ammonia, it gives good heat sensitization when a volume of 2 per cent, based on the volume of the latex, is used.

Among the organic complexes, the formate and acetate are particularly to be recommended because of their great heat-coagulating power.

Dicarboxylic amino acids give active compounds, but they are more troublesome.

Fat acids containing double bonds, of the type zinc-ammonium undecylenate or the oleate, have the advantage of being applicable to the manufacture of sponge rubber, for the complex, because of its surface-active properties, acts

both as a foaming agent and a heat-coagulating agent, and can be added at the moment of use or several hours earlier without difficulty.

Thus, the range of heat sensitizing agents of the zinc-ammonium complex type is, in fact, reduced to two or three practical effective agents, namely, the formate and the acetate in the manufacture of solid objects, and the oleate in the manufacture of molded sponge objects. The stearate often used is much less effective.

NOTES

We propose, for the preparation of the oleate compound, the following formula:

Zinc oleate	100 grams
Concentrated ammonia	100 cc.
Water (distilled or permuted)	100 cc.

Solution of the oleate is quite normal under typical conditions of ordinary practice; solution of the formate and acetate is normal provided that they are placed in a hermetically closed receptacle.

To latex already containing the vulcanizing ingredients, 1 to 3 per cent of this solution is added, according to the chemical stability of the latex. The mixture is then ready to be frothed. It is then poured into a mold of metal or plaster and put in an oven for 10 to 20 minutes at 100°, according to the nature and thickness of the mold. Vulcanization is usually carried out in boiling water.

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- ³ Lepetit, *Rev. gén. caoutchouc* **24**, 390 (1947); *Trans. Inst. Rubber Ind.* **23**, 104 (1947).
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- ⁵ This solution can be obtained only under hot conditions, since the solubility of zinc glycoollate is otherwise too low.

II. THE PROCESS OF HEAT SENSITIZATION OF DEGRADED LATEX

INTRODUCTION

We have already seen¹ that active heat-sensitizing agents of the zinc ammonium complex type number only a few representatives. Among the complex salts derived from the amino acids, only the dicarboxylic salts are at all effective on the heat sensitization of latex containing ordinary vulcanizing ingredients. We know that the degradation of proteins in latex by chemical, biochemical, or thermal means causes the formation of amino acids capable of forming zinc salts, only a few of which form ammonium salts¹, and, consequently complex zinc-ammonium salts.

What then is the nature of the amino acids present in the serum of a degraded latex, to what degree can their ionic influence explain the heat sensitivity of this latex, and how is the solubility of zinc oxide in the serum influenced by the presence of these acids? These are some of the questions which present themselves and which we shall try to answer.

ROLE OF AMINO ACIDS IN HEAT SENSITIZATION

Let us review, briefly, the results obtained by Lepetit² in his study of the problem of heat sensitization by the biochemical degradation of latex.

(1) A highly degraded serum² heat-sensitizes effectively a highly degraded cream.

(2) A serum which has not been degraded has only a slight effect on a highly degraded cream.

(3) A highly degraded serum has practically no heat-sensitizing effect on a cream which has not been degraded.

The attempt was made to explain these facts by applying more or less degraded creams, not with serums, but with aqueous solutions of various amino acids. These experiments were carried out by adding 5 grams of cream to 0.5 cc. of a 20 per cent aqueous solution of amino acid and 0.15 cc. of a 33 per cent dispersion of pure zinc oxide. The mixture, prepared in this way in a test tube, was put in a water bath at 70° C, and the time for coagulation to take place was noted.

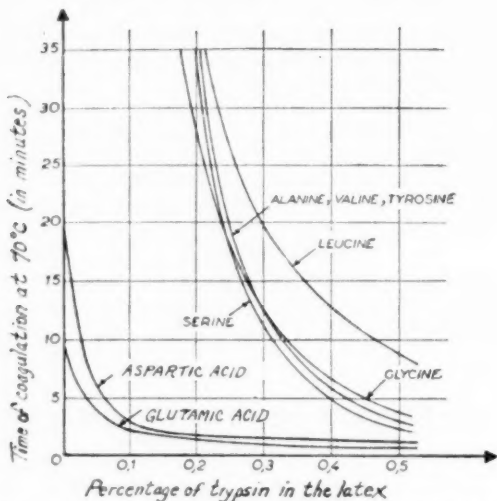


FIG. 1.—Heat-sensitizing effects of amino acids on creams from latex trypsinated to different degrees.

The heat coagulating powers of these acids correspond perfectly with the results obtained previously¹. Figure 1 shows clearly that the amino monoacids only act on highly degraded cream, whereas the amino diacids are effective on cream that has not been degraded.

If, instead of incorporating a solution of amino acid and a dispersion of zinc oxide in the different creams, we add directly the zinc salt in solution, the times for coagulation to take place are much shorter. Everything appears then to depend on the speed of solution of the zinc oxide.

DETERMINATION OF AMINO ACIDS IN SERUM

The fat acids with short chains have a rather well defined coagulating power, but their proportion in latex serum is very small. The potassium hydroxide index determined on the fat acids extracted by alcohol is less than 20 mg. per 100 grams of highly degraded serum. Only the amino acids can, therefore, be responsible for heat sensitization. Since these are divided into

two distinct groups according to their heat coagulating power, we decided to determine in what proportion these two types of acids are present in latex serum.

We shall not discuss any determinations carried out by the electrometric method⁴ in aqueous and non-aqueous mediums, because they proved to be very inexact. Our choice finally fell on the method of chromatographic analysis, with which it is possible to separate easily monocarboxylic amino acids from dicarboxylic amino acids.

CHROMATOGRAPHIC METHOD

Separation is carried out on an adsorbing column of alumina. After having eliminated all free and combined ammonia in the serum by adding the necessary quantity of sodium hydroxide⁵ for the purpose and by carrying the mixture to dryness carefully on a water bath, the residue is taken up with warm distilled water, and the solution is filtered on an alumina column especially prepared for the purpose. In the first filtrate, all the amino monoacids are recovered, while the diacids are adsorbed on the alumina. These are then eluted by 2 *N* hydrochloric acid. The amino acid content in each filtrate is calculated as nitrogen⁶.

TABLE I

	Serums			
	Normal	With 0.1% trypsin	With 0.5% trypsin	Old
Monoacids	0.029	0.070	0.083	0.048
Diacids	0.039	0.074	0.101	0.058
Nitrogen (amino acids)	0.068	0.144	0.184	0.106
Nitrogen (total)	0.093	0.142	0.184	0.107
Ratio $\frac{\text{diacids}}{\text{monoacids}}$	1.34	1.06	1.22	1.21

The results shown in Table I prove that, after elution with hydrochloric acid, nothing is retained by the alumina except in the case of serum of latex that has not been degraded, which contains a certain amount of peptides.

It is interesting to note also that, according to the state of degradation of the latex, there is a variation of the proportion of monoacids and diacids.

If the proportion of the various amino acids in a latex serum is known, without being able to reconstitute the amino acid medium synthetically, one can nevertheless approximate them rather closely by taking the two types of amino acid, glycolic and aspartic acid, in the proportions indicated by the analysis. If this pseudo-serum is added to the corresponding cream, we obtain a latex containing a synthetic serum.

A comparison of the heat sensitivity of a latex degraded by 0.1 per cent trypsin with that of cream equally degraded to which the corresponding synthetic serum has been added, gave the following values:

Time of coagulation at 70° C
Of degraded latex: 4 minutes
Of synthetic latex: 3.75 minutes

On the basis of these closely similar values, it can be concluded that the amino acid content of the serum of degraded latex can in itself explain, from an ionic point of view, the heat sensitivity of this latex.

ROLE OF ZINC OXIDE IN HEAT SENSITIVITY

Zinc oxide is indispensable to the heat sensitization of latex of the character which we have considered, for it is capable of furnishing positive ions, either in the form of zinc salts in the case of most mineral and organic acids, or in the form of complex zinc-ammonium ions in the case of amino monocarboxylic acids.

The heat sensitivity of a latex is, then, a function of the amount of zinc oxide solubilized and, consequently, on the rate of solubilization of the given zinc oxide. The amount of oxide solubilized depends on the nature of the serum, as has been shown by Wren⁷, and the rate of solubilization depends on the size of the particles of zinc oxide.

We had intended to measure this solubility of zinc oxide in the latexes studied previously, but in order for this measurement to retain any significance it was necessary to obtain values corresponding to the zinc actually solubilized at the moment of analysis. Since latex serum is a complex medium which the least change can upset (in general, equilibrium reactions, and in particular, the content of zinc solubilized), it was hardly advisable to use any ordinary method of chemical analysis. Polarography once again was of great use to us.

Although it is possible to determine zinc directly polarographically in concentrated latex, the presence of zinc oxide in the case of the degraded latex causes a thickening and often coagulation, making any measurements impossible after a few hours of contact with the zinc oxide. We were consequently obliged to make these analyses with serum. Since serum itself is an electrolytic medium containing a rather large proportion of ammoniacal salts in relation to the zinc which is solubilized, it was fortunately unnecessary to add an inert electrolyte, as is usually done, to cancel the effect of the diffusion current. We were then able to determine the zinc, without changing the composition of the serum, in the following way. To 4 cc. of serum is added 3 drops of a 30 per cent dispersion of zinc oxide. This mixture is put in a tightly stopped electrolytic cell, which is then agitated vigorously. To make the measurement, the cell is opened and put under the drop electrode. The cell is closed again immediately after the measurement, in order not to lose any ammonia. The cell is then kept at a constant temperature until the next determination.

MEASUREMENT OF SOLUBILITY OF ZINC OXIDE
IN VARIOUS SERUMS AT 20° C

Solubilization is quite rapid; consequently, at the end of one hour of contact, after only a single agitation at the moment of addition, four-fifths of the zinc oxide which is capable of dissolving is already solubilized, regardless of the nature of the serum.

TABLE II
QUANTITY OF DISSOLVED ZINC IN THE SERUMS OF LATEX
AFTER CONTACT FOR 24 HOURS WITH ZINC OXIDE
(grams per liter)

Concentration	Serums			Old
	Normal	With 0.1% trypsin	With 0.5% trypsin	
Normal	3.3	3.8	5.7	3.7
Diluted to $\frac{1}{4}$	1.5	1.8	2.4	1.0

If we compare the quantities of zinc dissolved in the different serums (see Table II), we observe that they increase with the degree of degradation of the latex. In the case of diluted serums, however, old latex dissolves the smallest quantity of zinc, although it is more heat sensitive, than ordinary latex. This shows clearly that the nature of the acids is different in the two latexes.

MEASUREMENT OF THE SOLUBILITY OF ZINC OXIDE
IN VARIOUS SERUMS AT 50° C

This measurement presented certain difficulties because of the influence of temperature on the height of the polarographic wave. We were able, however, to maintain the temperature within almost one degree during the few minutes necessary for the determination by using small electrolytic cells which were well heat insulated.

The results which are shown in Table III are rather unexpected. The solubility of zinc oxide is less at 50° C than at 20° C in all the serums. Returning to 20° and recommencing the measurement, one does not again obtain the original values, no doubt because of small losses of ammonia during the successive operations, but one does obtain greater solubility than at the higher temperature.

TABLE III
QUANTITY OF DISSOLVED ZINC
(grams per liter)

Serums from	24 hours' contact with zinc oxide at 20° C	After heating for 6 hours at 50° C	After the heated serum has stood 12 hours at 20° C
Normal latex	3.3	2.6	2.9
Latex with 0.1% trypsin	3.8	3.1	3.3
Latex with 0.5% trypsin	5.7	4.4	5.0
Old latex	3.7	2.9	3.25

There is thus a decrease of solubility of zinc oxide when hot, but although there is less zinc solubilized and, consequently, zinc ammonium complexes there are not necessarily fewer positive $\text{Zn}(\text{NH}_3)_4$ ions. The dissociation is not a function of the quantity of zinc solubilized, but of the temperature.

So in spite of the lower solubility of zinc oxide in hot serum, the greater dissociation is sufficient to liberate a large enough quantity of ions to bring about coagulation.

CONCLUSIONS

The heat sensitivity of a naturally or biochemically degraded latex is due in large part to the presence of amino diacids liberated by the degradation of proteins. These acids alone are capable of forming zinc ammonium complexes; however, in the case of a highly degraded latex, the monoacids with zinc oxide form soluble salts which are capable of heat coagulating this latex, the chemical stability of which has been much weakened by the desorption of the proteins.

The nature of the amino acids governs the solubility of zinc oxide and, consequently, the heat sensitivity of the latex under consideration.

In order to complete this work, we would have to determine the behavior of zinc-ammonium complexes in the phenomenon of coagulation, and study their dissociation in the latex. Does coagulation take place by simple neutralization of the negative particles of rubber by the $\text{Zn}(\text{NH}_3)_4$ cation, or rather, as is

believed by certain Dutch chemists, does the zinc hydroxide formed by dilution of the complex act in a particular colloidal state? The problem remains unsolved.

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- ³ The creams and serums were obtained by treating a 60 per cent latex with powdered hog pancreas rich in trypsin, and creaming with the aid of a 10 per cent solution of Alg-gum, then diluting the latex to about 4.
- ⁴ The description of these experiments will be found in the complete study which will be published soon. (Cassagne, "La thermosensitivité du latex d'hevea", Hermann & Cie., 1950.)
- ⁵ A preliminary determination of the acidity of the serum is necessary.
- ⁶ The nitrogen determinations were made according to the semi-micro-Kjeldahl method (norm AFNOR T 48-106).
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- ⁸ We cannot describe in detail here the principle and the technique of polarographic analysis without going beyond the scope of this article. We cite the work of Verdier ("Les principes et les applications de la méthode polarographique d'électroanalyse", Hermann et Cie., Paris, 1943) and Kolthoff and Lingane ("Polarography", Interscience Publishers, Inc., New York, 1941) for the principle of the method and its general applications.

PARTICLE SIZE OF RUBBER GLOBULES IN HEVEA LATEX *

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INTRODUCTION

According to Langeland¹ the number of particles per cc. of latex with a dry rubber content of 40 per cent amounts to $0.7 - 0.8 \times 10^{12}$; this number was determined by counting the particles in a specified volume of a suitably diluted latex by means of an ordinary microscope. Van Gils² used an ultramicroscope and found a number of 1.19×10^{12} per cc. of 40 per cent latex. The smallest particles which could be observed by Langeland had a diameter of about 0.2μ , as against 0.02 or 0.03μ diameter observable with an ultramicroscope.

A particle-size distribution was determined photographically by Lucas³, using ultraviolet light having a wave length of 2573 \AA and a microscope specially adapted to the use of this light. Particles having a diameter of at least 0.12μ can be made visible in this way, but his data (Figure 2) indicate the presence of a considerable number of particles below the visibility limit. These measurements were repeated by Hessels⁴ with visible light, which made observation of particles down to about 0.2μ diameter possible. According to Hessels, about 10 per cent of the particles have a diameter of less than 0.2μ , whereas this fraction has been found by Lucas to amount to about 60 per cent.

The considerable deviation between the results of van Gils and those of Langeland, suggests the presence of a fairly large number of particles smaller than 0.2μ . This conclusion is confirmed by Lucas and Hessels, and is in fair agreement with the results obtained by means of ultra-methods.

SIZE-FREQUENCY DISTRIBUTION

Consider a volume of latex containing a volume fraction V of rubber distributed over n_o particles; the number of particles having a radius r_i is called n_i . The volume-average radius r_v is then defined by:

$$r_v^3 \cdot n_o = \sum r_i^4 n_i = \frac{3}{4\pi} V \quad (1)$$

Similarly, a surface-average radius r_s is defined by:

$$r_s^2 \cdot n_o = \sum r_i^2 \cdot n_i = \frac{1}{4\pi} S \quad (2)$$

where S stands for the total surface of all rubber particles.

Values for these average radii are easily determined from a size-distribution curve, if an analytical expression can be found which describes the curve with sufficient accuracy. A suitable function, proposed by Dobrowsky⁵, can be

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written:

$$n_p \cdot dp = \frac{\alpha}{p^3} \exp \left(1 - \frac{1}{p} \right) \cdot dp \quad (3)$$

where $n_p dp$ is the number of particles having a size parameter between p and $p + dp$; p is defined by the relation $r_p = pr_o$; r_o is a suitable unit of length which may be considered as determining the position of the curve represented by Equation (3), and α is a constant which is only dependent on the total number of particles under consideration. The general shape of a size-frequency distribution curve which can be described by Equation (3) can be seen in Figure 1, where α has been put equal to 1.

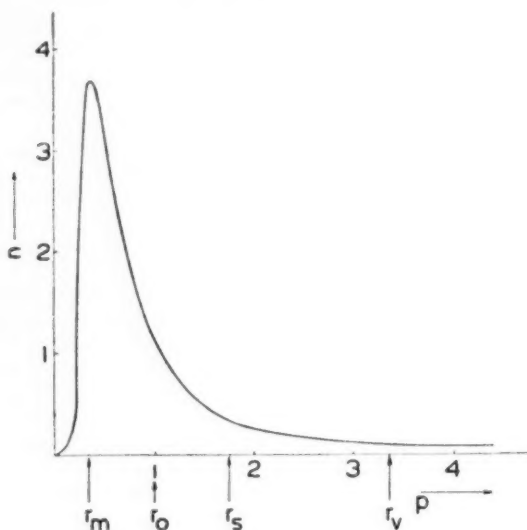


FIG. 1.—Size-frequency distribution according to Equation 3.

This expression (3) was originally proposed by Dobrowsky to describe the particle-size distribution of oil-in-water emulsions, but available data show that agreement with experimentally determined size-frequency distributions is unsatisfactory in this case. The size-frequency distribution curve for rubber globules in Hevea latex, as determined by Lucas, however, corresponds with the curve obtained from Equation (3), if r_o is taken as 0.13μ .

Comparison between experimentally determined distribution curves, and Equation (3) is facilitated by using integral distribution curves, defined by the relation:

$$f(p_1) = \alpha \int_0^{p_1} \frac{1}{p^3} \exp \left(1 - \frac{1}{p} \right) \cdot dp \quad (4)$$

where $f(p_1)$ represents the number of particles smaller than $(r_o \cdot p_1)$. The data of Lucas for two samples of latex, together with the curve obtained from Equ-

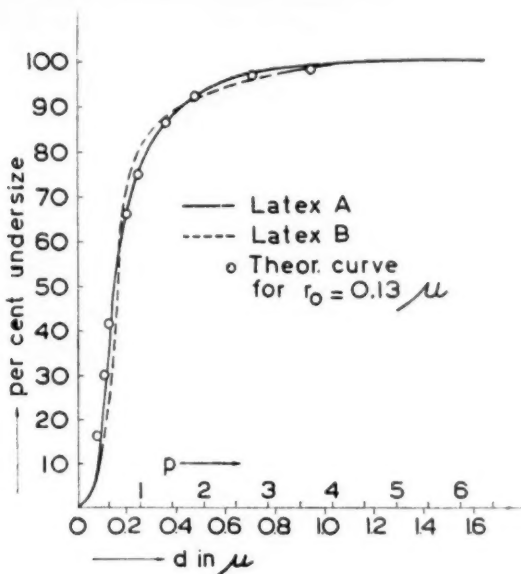


FIG. 2.—Size-frequency distribution of Hevea latex according to Lucas.

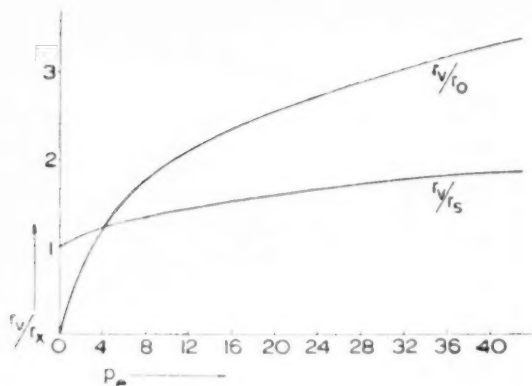
tion (4) with $r_0 = 0.13 \mu$, have been plotted in Figure 2. Agreement is satisfactory, especially in the case of latex A.

The expression (3) decreases in the region of the very large particles somewhat too slowly and this causes the total volume, and even the total surface of a finite number of particles, as calculated by means of this formula, to become infinite:

$$\begin{aligned}
 V &= \frac{\alpha}{3} \cdot 4\pi r_0^3 \int_0^\infty \sim \exp\left(1 - \frac{1}{p}\right) \cdot dp = \sim \\
 S &= 4\pi\alpha r_0^2 \int_0^\infty \sim \frac{1}{p} \cdot \exp\left(1 - \frac{1}{p}\right) \cdot dp = \sim
 \end{aligned}
 \tag{5}$$

This is not a very serious disadvantage, as experimental determination of the size-frequency distribution of emulsified oil globules has shown that a comparatively small number of very large particles which are always found to be present have a volume which is of the same order of magnitude as the total volume of all the small particles together. The few extremely large particles which cause the divergence in Equation (5) may be assumed to be non-existent in actual systems because these particles rapidly coalesce to form a separate oil layer. This means that the size-frequency distribution can be described by (3), where p is not allowed to become infinite, but remains below a fixed value called p_c .

A similar proposal has already been made by Dobrowsky, when he uses formula (3) to calculate the rate of creaming of emulsified oil droplets.

FIG. 3.—Ratio of radii as a function of p_e .

CALCULATION OF AVERAGE SIZE

The volume-average radius r_v , as given by (1):

$$r_v^3 \cdot n_0 = \sum_i r_i^3 n_i = r_o^3 \sum_i p_i^3 n_i$$

can be expressed in r_o , taking account of the condition that $p \leq p_e$. By integrating graphically:

$$\frac{r_v^3}{r_o^3} = \frac{\alpha}{n_1} \int_0^{p_e} \exp\left(1 - \frac{1}{p}\right) \cdot dp \quad (6)$$

with $n_1 = f(p_e)$ as given by Equation (4), the ratio between r_o and r_v is obtained as a function of p_e . This ratio, which is represented in Figure 3, appears to depend rather strongly upon the value of p_e .

A similar relation can be deduced for r_s , from which the practically important ratio r_v/r_s may be obtained. This is also shown in Figure 3, from which it follows that this last mentioned ratio depends much less on p_e . By varying p_e from 24 to 32, this ratio changes from 1.68 to 1.74; i.e., only 3.5 per cent.

The most frequently occurring radius can easily be calculated to be:

$$r_m = \frac{1}{3} r_o$$

It can be seen from Figure 3 that r_v may reach values as large as 7.5 to 9 times r_m , which appears to be much larger than has been assumed generally.

A survey of the relative magnitudes of the various average radii for $p_e = 40$ is given in Figure 1.

APPLICATION

A value of r_o having been determined by drawing a curve according to Equation (4) resembling as accurately as possible the experimentally determined integral distribution curve, r_v can be read from Figure 3 if p_e is known, or vice versa. The determination of van Gils gives a value for $r_v = 0.43 \mu$, from which $r_v/r_o = 3.3$ and $p_e = 40$. Application of the formulas to the size of oil globules of oil-in-water emulsions and of the fat globules in milk gives values for the ratio r_v/r_o , which never become higher than 1.5.

It would appear reasonable, then, to apply the formulas to Hevea latex.

If $p_e = 40$, the ratio $r_v/r_s = 1.9$, and $r_s = 0.226 \mu$, from which the interfacial area of 40 per cent latex is found to be $S = 7700$ sq. cm. per cc. of latex.

It would be desirable to compare these values with those obtained by other independent methods, such as an experimental determination of the total interfacial area.

A value of p_e cannot be obtained from a comparison of the experimentally determined integral distribution curve with the theoretical one, as the difference between these curves for values of p_e between 10 and 30 is far within the experimental error.

The calculations proposed in this paper are not suitable for the detection of small differences in specific interfacial area of various samples of latex. Thus, if a latex of known rubber content V is found to contain n particles per cc., the relative error in the determination of the interfacial area S can easily be calculated from:

$$V = \frac{4}{3} \pi r_v^3 \cdot n; S = 4 \pi r_s^2 \cdot n$$

Calling the ratio $r_v/r_s = Q$, this gives:

$$S = (4\pi)^{\frac{1}{3}} \cdot n^{\frac{1}{3}} \cdot (3V)^{\frac{2}{3}} \cdot Q^{-2}$$

hence:

$$\frac{S}{dS} = \frac{1}{3} \frac{dn}{n} + 2 \frac{dQ}{Q}$$

The ratio Q can hardly be determined with sufficient accuracy.

Comparison of experimental data obtained by various authors using different methods was made difficult by the strongly asymmetrical shape of the size-frequency distribution curve of Hevea latex. The experiments of Wren⁶ may be cited as an example. By spreading a "monolayer" of latex globules upon an aqueous substrate and compressing this layer until a fairly sharp increase in pressure resulted, Wren determined an average thickness of the close-packed layer of about 0.9μ . The measurements of Lucas, as interpreted by Wren, would have predicted an average thickness of only 0.44μ , which caused Wren to assume that the latex used by him contained much larger globules than the latex which had been investigated by Lucas.

Consider a monolayer containing n globular particles, all lying with their centers in one plane, and having a total volume:

$$V = \frac{4}{3} \pi \sum_i r_i^3 \cdot n_i = \frac{4}{3} \pi r_s^3 n$$

The total surface occupied by these particles equals the sum of their cross-sections:

$$s = \pi \sum_i r_i^2 n_i = \pi r_s^2 n$$

If the particles are assumed to be in a state of closest packing, where every interstice between adjacent particles is completely filled with smaller particles, the average thickness of the layer thus obtained would be:

$$d = \frac{V}{s} = \frac{4}{3} \left(\frac{r_v}{r_s} \right)^2 \cdot r_v = 1.9 \mu$$

The state of closest packing is determined experimentally by compressing the layer until the surface pressure shows a sudden increase. Up to this point, compression causes a mutual approach of the particles, and only small repulsive forces have to be overcome. From this point onward, however, a further decrease in area causes a strong increase in the repulsive forces either because now the double-layer surrounding each particle has to be distorted or some particles have to be forced out of the monolayer.

It may be expected that a state of closest packing, as defined above, will not be reached because a number of interstices between the larger particles will remain unfilled. Moreover, some of the nonrubber constituents of the serum probably occupy some of the space available on the surface. This causes the surface pressure to increase already at an average film thickness smaller than the calculated value of 1.9μ . The value of 0.9μ obtained by Wren shows that, actually, a state of rather loose packing results, and is certainly not inconsistent with the data of Lucas.

CONCLUSIONS

1. The use of visible light in determining the average particle size or the particle-size distribution in Hevea latex renders the results meaningless, as only about 40 per cent of the particles have a diameter of more than 0.2μ .

2. In considering the size-frequency distribution curve as determined by Lucas, it could be assumed that, actually, the number of particles having a diameter of less than 0.12μ might be very much larger than has been indicated by him. The agreement with the determination of the number of particles by van Gils, however, may be taken as evidence in favor of the correctness of the curve as given by Lucas⁷.

3. An expression has been given which describes the size-frequency distribution curve, as found by Lucas, with a high degree of accuracy. It is necessary to assume that no particles larger than 5.2μ are present in the latex.

4. Attention is directed to the considerable difference existing between the various average diameters, caused by the strongly asymmetrical shape of the size-frequency distribution curve.

This work forms part of the program of fundamental research on latex problems undertaken by the Research Department of the Rubber-Stichting, Delft, under the management of H. C. J. de Decker.

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EVALUATION OF TREAD WEAR *

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The rate of wear of a tire in service depends primarily on the design of the tire, the properties of its components, and the conditions to which it is subjected in service. This implies that problems of tire design and development are very complex, as must be well realized by those engaged in this type of work.

The degree of success that can be achieved in tire development will, to a certain extent, depend on the availability of a simple and reliable method of analyzing experimental measurements on tire wear. In fact, great value would lie in a method that could serve as an industry standard.

It has been the common practice to use as a tire rating the last available measurement of miles per 0.001 inch of tread wear in a tire test. The practice has a definite disadvantage in that considerable emphasis is placed on the last measurement, and all measurements prior to the last are disregarded. Furthermore, such a rating may be unreliable, as it may, and in general does, vary with mileage.

A method has been developed in which all experimental measurements of nonskid depth taken during a test run are incorporated in a single rating of tread wear for each tire tested. Essentially, the method consists of the utilization of a certain functional relationship between nonskid loss and mileage.

METHOD OF ANALYSIS

The proposed method of analyzing tread wear measurements is based on the hypothesis, substantiated by results gathered during 2.5 years, that the mathe-

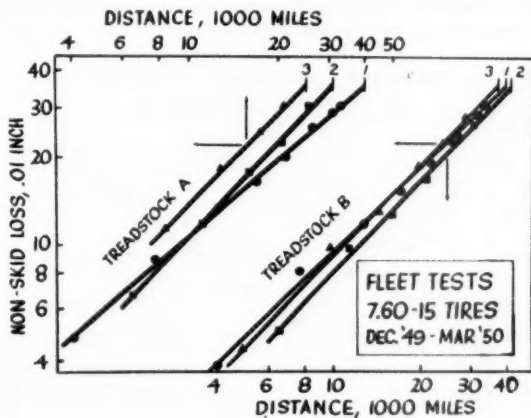


Fig. 1.

* Reprinted from *Analytical Chemistry*, Vol. 23, No. 11, pages 1641-1646, November 1951. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its 58th meeting, Washington, D. C., February 28-March 2, 1951.

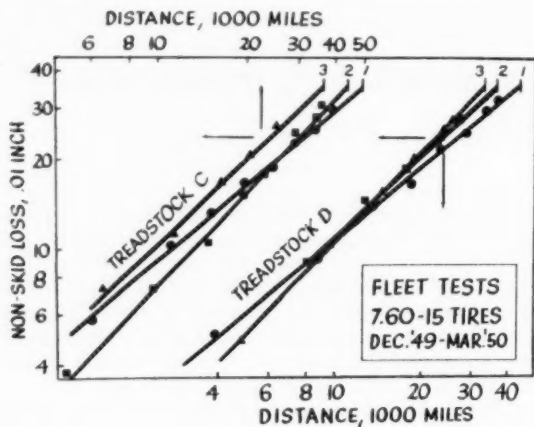


FIG. 2.

mathematical relationship of nonskid loss, y , or the decrease in nonskid depth from its initial value, to distance x over which the tire has been tested is of the power type:

$$y = ax^b$$

Plotted on log-log graph paper, y versus x is thus a straight line (see Figures 1 through 8). Constants a and b can be determined from the experimental data by means of a linear regression of $\log y$ on $\log x$ using the method of least squares. a and b define wear-resistance properties of a particular tread stock in a tire of given design under given conditions.

If it is desirable to have a single rating, one of several may be used:

1. Mileage to baldness—that is, to the point on the regression line at which total nonskid loss is equal to the initial nonskid depth.

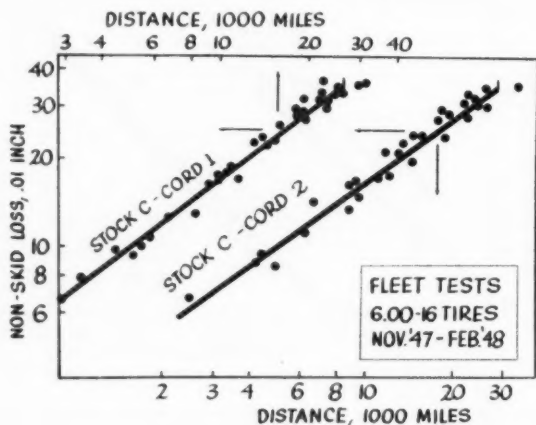


FIG. 3.

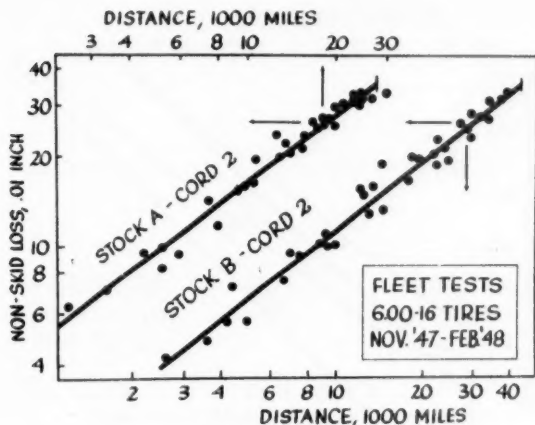


FIG. 4.

2. Miles per 0.001-inch nonskid loss at baldness—that is, mileage to baldness divided by the initial nonskid depth in thousandths of an inch. In a relative evaluation of tires, this rating allows the comparison of mileages to baldness compensated for any differences in initial nonskid depths that may exist.

3. Amount of nonskid loss, taken from the regression line, at an arbitrarily chosen mileage. It is best to use a figure based on a relatively high mileage.

APPLICATIONS OF METHOD

The proposed method of analysis has been applied to a large variety of tires in a great number of widely different types of evaluations. Examples of some of these are listed in Table I, including both fleet and field service tests. Some information on test conditions may be of interest.

Fleet tests were conducted by the tire test fleet of the Gates Rubber Co. in

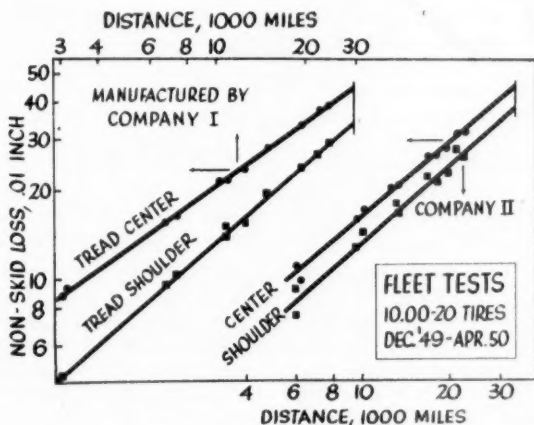


FIG. 5.

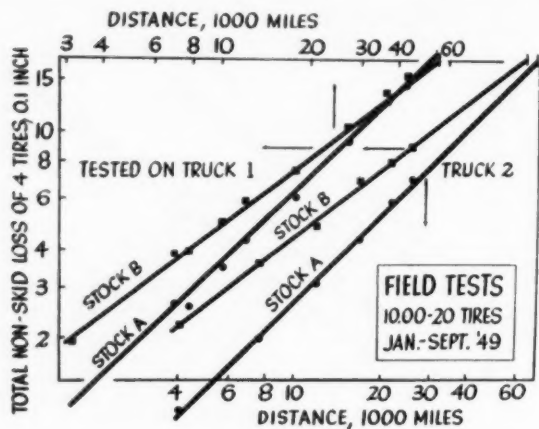


FIG. 6.

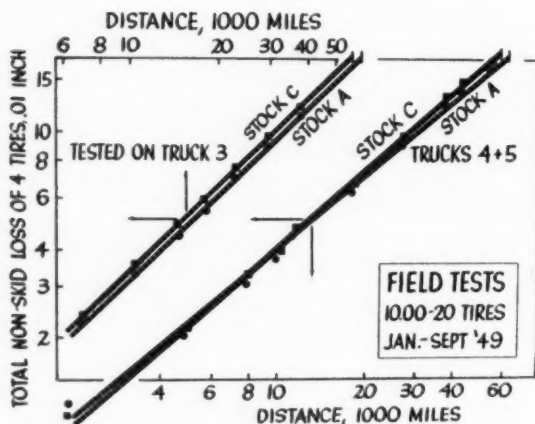


FIG. 7.

TABLE I
DETAILS OF SOME TREAD WEAR TESTS

Figure	Type of test	tire size	Tested at % of rated load	Initial tire pressure (lb./sq. in.)	Test period	Test variables
1 and 2	Fleet	7.60-15 low pressure	114	24	Dec. '49-Apr. '50	Tread stocks
3 and 4	Fleet	6.00-16	132	28	Nov. '47-Feb. '48	Tread stocks and tire cords
5	Fleet	10.00-20	145	70	Dec. '49-Apr. '50	Competitive tires; different tire designs, stocks, cords, etc. Tread center and shoulder wear evaluation
6 and 7	Field service: tractor-trailer transports	10.00-20	Varying	70	Jan. '49-Sept. '49	Tread stocks in half-and-half tires
8	Field service: taxicabs	6.50-15	Varying	Varying	Oct. '50-Nov. '50	Camelback stocks containing breakout material

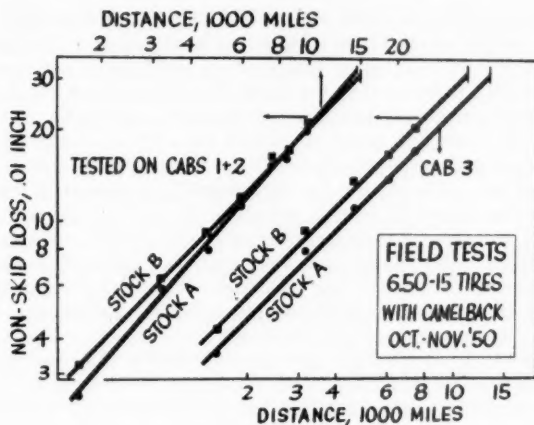


FIG. 8.

Arizona from November 1947 to April 1950. Driving speeds are 60 miles per hour in the daytime and 50 miles per hour at night for passenger cars, and 50 miles per hour day and night for trucks. Inflation pressures are checked periodically. Tires are usually tested at certain loads above rated loads. Passenger cars are weight-compensated to give equal loading on all four wheels, among which tires are rotated approximately every 1700 miles. On trucks, rotation is among drive wheels only. All wheels are checked for alignment weekly. The highest and lowest atmospheric temperatures of each day along the paved course are recorded; the averages of these over the duration of a test give some indication of the temperature conditions of the test. Nonskid depth is measured every 1700 miles to the nearest 0.001 inch at several equidistant points around the tire.

The field-service tests on tractor-trailer transport were conducted in the Kansas City area primarily on paved highways. Tires were rotated about every 5000 miles among the drive wheels only. The field tests on taxicabs were made in the Denver area under any but controlled conditions.

The data of these evaluations are shown graphically in Figures 1 through 8, together with their regression lines. For the great variety of conditions and variables shown in Table 1, the log-log graphs of nonskid loss *vs.* mileage are linear to a very high degree.

No denial of this linearity has been found in the great volume of tire testing that has been conducted in 2.5 years by the Gates Rubber Co.

This linearity is the basis for the proposed method of analysis of nonskid loss mileage data in evaluations of tread wear.

ANALYSIS OF GRAPHS

Mileages to baldness were computed for the data of Figures 1 through 8, and are indicated by short vertical lines at the upper ends of the regression lines. A discussion of a comparison of bald mileages to determine statistically significant differences is given at the end of this paper.

Some facts about these regression lines should be noted, because they may suggest interesting investigations of tire road wear.

In Figures 1 and 2, three tires of each of four stocks were tested. For each stock, the second tire was tested at a higher mean atmospheric temperature than the first, and the third at a higher temperature than the second (see Table II). The results seem to indicate that the lower the temperature, the less the slope of the regression line, and the greater the mileage to baldness.

Figures 3 and 4 are of a tread stock and tire cord evaluation. Each combination of stocks and cords was tested in six tires. Mean atmospheric temperatures varied very little during the test period. A statistical comparison of the bald mileages of stock C, cord 1, and stock C, cord 2, is given below.

In Figure 5 two tires of each manufacturer were tested. Nonskid loss readings were obtained in the center as well as shoulder regions of the tread. Both were plotted as straight lines on log-log paper. Figure 5 gives an indication of the uniformity of wear across the tread: The company I tires wore less evenly, as the slopes of the center and shoulder lines are different. Furthermore, the company I tires had considerably more nonskid left in the tread shoulder area when the tread centers were bladed than the company II tires.

In Figures 6 and 7 the total nonskid loss of the four drive wheel tires of each truck was plotted against mileage. The regression lines for truck 1 illustrate how misleading a rating of miles per 0.001-inch nonskid loss taken at 15,000 or 20,000 miles can be, for at such points stock A appears to be definitely superior to B, whereas actually both had about the same bald mileage. Truck 2 showed a similar large difference in slopes between stocks A and B. The

TABLE II
SUMMARY OF TEST RESULTS

Figure	Test variables	No. of tires tested	No. of points	Mean atm. temp. (° F)	Constants of regression line		Orig. NS depth, 0.001 inch	Bald mile- age, 1000 miles	Mi./ 0.001 at bald- ness
					A	b			
1 and 2	Stock A	1	8	52	-0.8399	0.8665	358	40.60	113.4
		1	5	57	-1.0447	1.0672	357	31.40	88.0
		1	4	60	-0.9056	1.0415	359	25.26	70.4
	Stock B	1	8	52	-0.9807	0.9595	357	39.64	111.0
		1	6	58	-1.1533	1.0611	357	40.52	113.5
		1	6	62	-1.0890	1.0527	360	36.56	101.6
	Stock C	1	8	54	-0.8709	0.8382	356	49.76	139.8
		1	8	58	-1.1703	1.0487	358	44.07	123.4
		1	5	62	-0.9216	0.9446	357	36.37	101.9
	Stock D	1	8	53	-0.7985	0.8252	258	43.55	121.6
		1	5	62	-0.8948	0.9358	356	35.53	98.7
		1	6	62	-1.0161	1.0371	359	32.73	91.2
3 and 4	Stock C, cord 1	6	34	50	-0.5256	0.7596	360.0	26.56	73.8
	Stock C, cord 2	6	33	51	-0.4910	0.7180	356.5	28.24	79.2
	Stock A, cord 2	6	35	50	-0.5316	0.7549	357.7	27.38	76.5
	Stock B, cord 2	6	30	51	-0.7135	0.7750	267.8	45.15	129.6
5	Tread center, Co. I	2	11	58	-0.6300	0.8425	444.5	29.54	66.5
	Tread shoulder, Co. I	2	10	58	-0.7503	0.8754	531.5	—	—
	Tread center, Co. II	2	11	60	-0.3886	0.7049	451.0	33.61	74.5
	Tread shoulder, Co. II	2	11	60	-0.7418	0.8663	497.5	—	—
6 and 7	Stock A, truck 1	4	9	—	-0.4185	0.9662	1819	54.58	120.0
	Stock B, truck 1		9	—	-0.0772	0.7686	1817	54.84	120.7
	Stock A, truck 2		6	—	-0.5867	1.0082	1824	68.03	149.2
	Stock B, truck 2		6	—	-0.1355	0.7804	1825	61.63	135.1
	Stock A, truck 3	4	8	—	-0.4634	0.9640	1821	61.41	134.9
	Stock C, truck 3		8	—	-0.4472	0.9698	1811	57.32	126.6
	Stock A, trucks 4 and 5		10	—	-0.2321	0.8334	1826	61.96	135.7
	Stock C, trucks 4 and 5		10	—	-0.2607	0.8610	1818	53.80	128.3
	Stock A, cabs 1 and 2	1	7	—	-0.8530	1.1636	316	14.57	46.1
	Stock B, cabs 1 and 2	1	7	—	-0.7349	1.0520	315	14.87	47.2
	Stock A, cab 3	1	5	—	-0.6326	1.0056	317	13.41	42.3
	Stock B, cab 3	1	5	—	-0.5579	1.0134	319	10.98	34.4

evaluation of stocks A and C on trucks 4 and 5 resulted in data that scattered more from the regression lines than similar data on truck 3 alone. This is probably due to the fact that a test made on only one vehicle is a better controlled test than one made partly on one and partly on another vehicle. In spite of this, and in spite of the crossing lines of trucks 4 and 5, the bald mileages fall in the same relative position in the two cases.

Figure 8 pertains to tests of camelback (recapping material) containing breakout material for increased traction on snow-covered roads. Here the tests on cabs 1 and 2 seem to show considerably less difference in bald mileage of the two stocks than that on cab 3. The above remarks on tests conducted partially on one and partially on another vehicle apply here as well.

SIGNIFICANCE OF WEAR-MILEAGE RELATION

The question may be asked: Why should the nonskid loss-mileage curve be of the power type? A satisfactory answer cannot be furnished. If nonskid loss y is plotted against mileage x on linear graph paper, a curve passing through the origin results. Mathematically y would increase without limit as x does. The curve would be concave toward the x -axis or toward the y -axis, depending on whether constant b is less or greater than unity, implying a decreasing or increasing rate of wear, respectively, as the test progresses. In most cases it was found that b is less than unity (see Table II), which means a decreasing rate of wear. This may be due to an increase in tread contact area caused by the growth of the tire, and to the geometry of the tread pattern and voids. Changes in tread radius during the test and in the tread movement pattern on the road may be partly responsible. Another possible factor is a change in abrasion resistance of tread stocks with time on test due to possible continued vulcanization, oxidation, and other effects.

The increasing rate of wear in the case of camelback containing breakout material is probably due, at least in part, to a decreasing contact area as breakout material is lost, and possibly to a decrease in abrasion resistance.

In the evaluation reported in Figures 1 and 2 the change in b from less than to greater than unity with an increase in mean atmospheric temperature is probably due to a change in the abrasion resistance.

STATISTICAL ANALYSIS OF TIRE WEAR

Linear regression.—The constants, a and b , in the relationship $y = ax^b$, which may also be written $\log y = \log a + b \log x$, where y is nonskid loss and x is mileage, can be determined from a linear regression of $Y = \log y$ on $X = \log x$ according to the equations:

$$\begin{aligned} A = \log a &= (\Sigma Y \Sigma X^2 - \Sigma X \Sigma XY) / D_X \\ b &= (n \Sigma XY - \Sigma X \Sigma Y) / D_X \\ D_X &= n \Sigma X^2 - (\Sigma X)^2 \end{aligned}$$

where n = number of pairs of values of X and Y .

Constants A and b reported in Table II were determined for y expressed in 0.1 inch and x in 1000 miles. Thus in the case of the first tire reported in the table:

$$\log y = -0.8399 + 0.8665 \log x$$

When $x = 1$, or 1000 miles, $y = \text{antilog } A = \text{antilog } (-0.8399) = 0.1446$, or 0.015 inch.

In Table II in the case of Figures 3 to 7 data for several tires in each case were pooled. Where tread stocks, tire constructions, etc., are to be compared, individual regressions will have to be made for each tire, as explained below.

It is recommended that the first rotation cycle, in which a tire has been run once on each of the several wheel positions, be considered as a break-in cycle. Data obtained subsequent to the break-in cycle are then to be used in the regression. It is best to use a number of datum points which is a multiple of four, if rotation is among four positions, so that there is equal representation among positions. The distances covered for each position should be over the same test course and of equal length. Furthermore, it has been the practice to start any passenger tire test on front positions, using dummy tires on rear positions, until the time of the first rotation for a particular vehicle.

Mileage to baldness.—After A and b have been determined, the mileage to baldness, x' , can be computed from $\log x' = (\log y' - A)/b$, where y' is the initial tread depth. If desired, and this may be preferable, y' may be defined as the initial tread depth minus an arbitrary depth such as 0.050 inch, in which case the tire would be considered bald when a tread depth of 0.050 inch has been reached.

It is common practice to measure tread depths at the same ten points (in the center void, or alternately on either side of the center rib) equally spaced around a tire throughout a test. The average of these ten readings is then computed for each mileage. The bald mileage determined from these is then a function of the average appearance of the tire.

If, in a certain test, four tires of the same population have been tested on the same car under identical driving and road conditions, then limits of uncertainty of the mean bald mileage can be computed from the four individual values. The method for doing this is given by the American Society for Testing Materials¹.

Differences in mileages to baldness.—In comparative tests of two different tread stocks under the same controlled conditions, such as in a half-and-half tire, or tires on test with frequent periodic rotation on the same car with the same driver over the same period of time, the question may arise whether the difference in bald mileages is great enough to be statistically significant. Or, what is the probability that the ratings of two tread stocks, in terms of bald mileages, could be estimates of identical true or objective values?

The authors have found that, in many testing programs, a statistical t test for paired variates can answer the question. An example would probably explain this best.

In the testing illustrated in Figure 3 and 4, four tire constructions were investigated. A set comprised of one of each of the four constructions was tested on each of three cars over the same test course and over approximately the same time interval with periodic rotation. Subsequently, another set was tested in a

TABLE III
COMPARISON OF TWO TIRE CONSTRUCTIONS

Car	Time period	Bald mileages for tire constructions		Differences in bald mileages
		C-1	C-2	
1	1	23,360	23,120	-240
	2	25,150	24,860	-290
2	1	28,410	32,010	3600
	2	34,350	33,300	-1050
3	1	25,060	26,640	1580
	2	23,200	27,280	4080

similar manner on each of the cars. Weather and road conditions as well as the effects of car and driver were, therefore, the same for each set of four tires.

Thus, in order to compare two of the constructions, such as C-1 and C-2, a *t* test for paired variates is in order. Table III shows the bald mileages computed as explained above for each of the six tires of each construction tested, as well as the differences in bald mileages of C-1 and C-2. The mean difference, \bar{d} , is 1280 miles. The standard error of this mean is:

$$\left[\frac{\Sigma(d - \bar{d})^2}{n(n-1)} \right]^{1/2} = \left[\frac{n\Sigma d^2 - (\Sigma d)^2}{n^2(n-1)} \right]^{1/2} = 885 \text{ miles}$$

Here *n* is the number of differences; in this case 6. Now the mean divided by its standard error is $\frac{1280}{885} = 1.446$. For \bar{d} to be significantly different from zero, the mean divided by the standard error would have to be 2.571 or greater. This value is taken from a table of Student's *t*, available in numerous texts on statistics² for *n* - 1 = 5 degrees of freedom and a probability level of 0.05. As 1.466 is less than 2.571, the conclusion is that the available data do not indicate any significant difference in means for tire constructions C-1 and C-2. In fact, the probability of no difference lies between 0.20 and 0.30. It has been generally accepted that for a significant difference this probability must be less than 0.05.

The bald mileages of Table III were computed from all available data, up to about 23,000 miles. If bald mileages are computed on the basis of eight datum points (beyond the initial break-in cycle), in this case up to about 12,000 miles, a *t* test for paired variates leads to the same conclusion as above—that is, no significant difference in C-1 and C-2, the probability of no difference being between 0.50 and 0.60. If this process is repeated for 12 and 16 datum points, up to about 17,000 and 21,000 miles, respectively, the probability of no difference is between 0.20 and 0.30.

Furthermore, for each tire the differences in bald mileage based on eight points and based on all the available points were computed. The average difference was 1400 miles, and on test was not shown to be significantly different from zero. When this procedure was repeated for 12 and 16 points, the average differences were 560 and 180 miles, respectively, and both were not shown to be significantly different from zero.

Thus little was gained in testing tires beyond the first 8 to 12 datum points after the break-in cycle, other than somewhat more accurate estimates of the bald mileages.

Tire wear can be measured in several ways. Some investigators³ have expressed tire wear in terms of rate of wear and analyzed variance of the data to isolate the effects of tread compounds, tires, rotation cycles, rubbers, blacks, vehicle, wheel position, test conditions, and various interactions of these effects. Tests were designed to allow such analyses to be made. Much can be learned about the wear of tires and the effect of test conditions if data are analyzed in this manner.

It is the authors' opinion that mileage to baldness is another valuable measure of tire wear, especially in view of the fact that the user of tires judges not only on the basis of rate of wear by examining his tires periodically, but also, and possibly primarily, on the basis of the distance he can cover before his tires are bald.

If tires are tested to the point where the tread depth is 0 or 0.050 inch, whichever is desired, the bald mileage can be measured directly, in principle. In

practice, it is difficult thus to measure bald mileage directly, because tread depths are usually obtained at certain specified intervals. Interpolation or extrapolation may be necessary. There are a number of ways in which this could be done. It is the authors' opinion, based on experience, that the use of a power type of curve is one effective way, which also allows determination of bald mileage from a test discontinued prior to baldness. It is obvious that this analysis is based on the hypothesis of a power-type relationship between tread loss and mileage. This can be justified only on the basis of the examination of a large number of diverse cases.

Instead of determining the average bald mileage, it is possible to obtain a total of ten values for each tire, one for each point at which measurements are made. A measure of the variance around one tire, which also includes experimental errors of measurement, can thus be obtained. The magnitude of experimental errors can be obtained by making several sets of measurements around each tire. An analysis of variance could then be performed to determine the effects of tread compounds, the variation of tires of the same tread, variations within a tire, experimental errors, and possible interactions.

The extent to which one should go in obtaining and analyzing tread wear data depends to a great extent on the magnitude of the differences to be measured. In general, the smaller these differences, the greater the amount of replication needed, and vice versa.

CONCLUSIONS

The observed existence of a linear log-log relationship between nonskid loss and mileage in a great number of widely different types of tests may be exploited in order to realize substantial savings in the road testing of tires for tread wear. In many evaluations it is common practice for the Gates Rubber Co. to test tires to one half initial nonskid depth or to some arbitrary mileage only. The regression line and mileage to baldness are then determined. Of course, the greater the amount of data, and the more accurately controlled the conditions of testing, the more reliable will be the mileage to baldness. If in tread wear evaluations tests were terminated prior to baldness, about \$180 could be saved for each passenger tire tested, and \$490 for each truck tire, for every 10,000 miles. One investigation, to determine the effect of three different tire designs on tread wear, was made at a total cost of \$2200. If all tires had been tested to baldness, the cost would have been approximately \$4600.

In comparison with former common practice, the application of the proposed method of analysis of tire wear measurements can result in more reliable tread wear evaluations, more economical utilization of the tire test fleet, and a more rapid turnover of ideas.

ACKNOWLEDGMENT

The authors wish to thank the Gates Rubber Co. for the privilege of publishing this paper.

Since presentation of this paper it has come to the authors' attention that the method of analysis presented has also been investigated and proposed for both service and laboratory tests by J. M. Buist of Imperial Chemical Industries, Ltd⁴.

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MIGRATION OF MATERIALS DURING ACCELERATED AGING BY THE OXYGEN PRESSURE METHOD *

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The oxygen-pressure method of accelerated aging is well established among the test techniques used by the rubber industry. A great deal of work has been done in evaluating the effect of various factors which influence the data¹ and standard procedures have been established². In spite of this, variations which are beyond normal experimental error still occur, especially when unlike stocks are aged together in a bomb. As a result of this type of discrepancy, this investigation was undertaken.

Several workers³ have recognized the fact that when a heterogeneous group of stocks is aged in a single bomb, some materials migrate from one stock to another and act to change the apparent age resistance of all the stocks in the group. This action may serve either to increase or decrease the apparent resistance of oxidation, depending upon the nature of the migratory material and the stocks involved. A search of the literature on the subject failed to disclose specific materials which show this effect or the extent to which the migration affected physical properties.

This work shows that migration is not limited to any one material and that the effects on the stocks are large enough to cause significant errors in test data. Because a primary purpose of an accelerated aging test is to rate the relative resistance to oxidation which is afforded to a stock by an antioxidant, the majority of the data in this report are concerned with antioxidant migration. However, the data show that materials such as sulfur, accelerators, and copper salts also migrate and change apparent age resistance. It is probable that the migratory tendencies are not limited to the relatively few materials mentioned in this report, but these are representative and probably cause the most drastic changes in physical properties. A very extensive investigation would be necessary to classify all compounding materials into migratory or nonmigratory groups.

TEST METHODS

All aging was carried out in Bierer-Davis oxygen bombs² for 48 hours at 80° C under 300 pounds per square inch oxygen pressure. Six samples of each stock were aged under each condition, unless otherwise noted. All samples were from the same mix and the same cure. The bomb chambers were thoroughly cleaned to remove any residual material from previous tests. Each stock was aged alone in the bomb and also in combination with other stocks. Tensile strength, per cent elongation, and Shore A durometer values were obtained.

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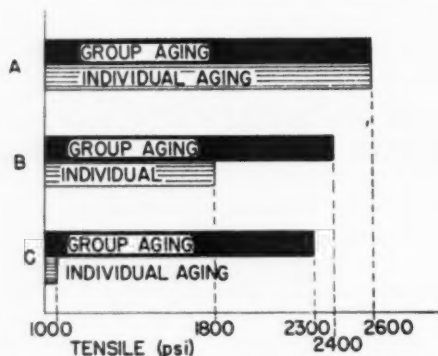


Fig. 1.—Comparison of group and individual aging characteristics of typical natural rubber tread formulation. Three different antioxidants.

ANTIOXIDANT MIGRATION

Figure 1 shows the age resistance of a group of natural rubber tread-type stocks, identical except for antioxidant. To assure that the differences in data were not due to accidental testing variations, repeated tests were made from a single mix and cure of each stock. Sixty-nine samples of each stock were aged in small groups of three or four samples to a bomb, then twenty-three samples were aged in groups containing all three stocks (Table I). The three stocks showed but slight difference in apparent age resistance when aged as a group,

TABLE I
GROUP AND INDIVIDUAL AGING

	A	B	C
Rubber	100	100	100
ZnO	4	4	4
Pine tar	2.4	2.4	2.4
Stearic acid	2.9	2.9	2.9
Santocure	0.45	0.45	0.45
Sulfur	3	3	3
Antioxidant 1 ^a	1	—	—
Antioxidant 2 ^b	—	0.25	—
Antioxidant 3 ^c	—	—	0.25
EPC black	42.5	42.5	42.5
Tensile to break (lb. per square inch)			
Group aged	2600	2400	2300
Aged alone	2600	1800	1000
Elongation to break (%)			
Group aged	450	450	450
Aged alone	450	420	350
Shore durometer values			
Group aged	55	54	50
Aged alone	55	51	44

^a Diphenyl *p*-phenylenediamine and phenyl-1-naphthylamine.

^b *p,p'*-Diaminodiphenylmethane (purchased as commercial antioxidant).

^c *p,p'*-Diaminodiphenylmethane (purchased as pure material).

60 minutes at 280° F.

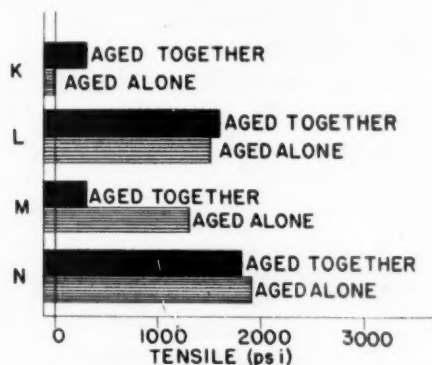


FIG. 2.—Comparison of group and individual aging characteristics of four gum rubber stocks. Different types and amount of antioxidant.

but when aged in individual bombs a significant difference between stocks was evident.

The antioxidants in stocks B and C of Figure 1 are reportedly the same material, *p,p'*-diaminodiphenylmethane. Stock B uses the material purchased as a commercial antioxidant and stock C uses the pure chemical. There are real differences in antioxidant effect between the two, which may be explained by the fact that impurities or additives in small proportions may have made the commercial antioxidant more effective.

TABLE II
GROUP AND INDIVIDUAL AGING

	K	L	M	N
Rubber	100	100	100	100
ZnO	5	5	5	5
Stearic acid	0.25	0.25	0.25	0.25
Sulfur	2.2	2.2	2.2	2.2
Tetraethylthiuram disulfide	1	1	1	1
Antioxidant 4 ^a	—	1	—	—
Antioxidant 5 ^b	—	—	1.5	—
Antioxidant 6 ^c	—	—	—	1
Tensile to break (lb. per square inch)				
Original	2650	2475	2250	2150
Group aged	300	1600	300	1800
Aged alone	Melted	1500	1350	1900
Elongation to break (%)				
Original	805	820	850	820
Group aged	400	710	430	780
Aged alone	Melted	680	680	720
Shore durometer values				
Original	31	30	30	29
Group aged	23	30	25	27
Aged alone	Melted	33	30	31

^a Reaction product of diphenylamine and acetone.

^b Alkylated phenol sulfide.

^c Phenyl-2-naphthylamine.

30 minutes at 300° F.

TABLE III
AGING CHARACTERISTICS OF FOUR STOCKS

	D	E	F	G
Rubber	100	100	100	100
ZnO	5	5	5	5
Stearic acid	0.25	0.25	0.25	0.25
Sulfur	2.2	5	—	0.60
Tetraethylthiuram disulfide	1	—	3	0.50
Benzothiazyl disulfide	—	1	1	1
Antioxidant 4 ^a	3	1	1	1
Tensile to break (lb. per square inch)				
Original	3500	3950	2600	3250
Aged alone	1000	2250	2100	2850
Aged with D	—	2150	2800	2900
Aged with E	900	—	1450	3300
Aged with F	1200	2700	—	1375
Aged with G	1850	2600	2375	—
Elongation to break (%)				
Original	730	730	680	760
Aged alone	490	560	530	700
Aged with D	—	560	580	695
Aged with E	450	—	510	740
Aged with F	530	550	—	590
Aged with G	600	580	580	—
Shore durometer values				
Original	35	35	34	33
Aged alone	32	39	37	33
Aged with D	—	37	37	32
Aged with E	32	—	37	34
Aged with F	30	40	—	35
Aged with G	31	38	38	—

^a Reaction product of diphenylamine and acetone.

15 minutes at 300° F.

Ignoring possible synergistic effects between antioxidants, it appears that antioxidant 1 was much more active than either 2 or 3, and was present in sufficient quantity to lend additional protection through migration to stocks B and C when all three were aged together and thus give them an artificial aging value. If the three stocks had been evaluated by the "group aged" data alone, the conclusions would have been erroneous and could have caused serious difficulty in service life of the end product.

A group of gum stocks, identical except for type and amount of antioxidant, was also aged singly and as a group (Figure 2 and Table II). The data show large discrepancies in results as a consequence of the practice of placing unlike stocks together in a bomb.

Stocks K and M show no difference in their apparent age resistance when aged together. When aged alone, stock K melted and stock M retained about 60 per cent of its original properties.

Apparently the antioxidants from one or more of stocks L, M, and N migrated to the stock not protected by antioxidant (K) when all four were exposed together in the bomb.

In Figure 2, stock M shows less apparent aging resistance when aged with other stocks than when aged alone. Possibly this antioxidant was nearly consumed by the parasitic action of stock K, the unprotected stock and, as a result,

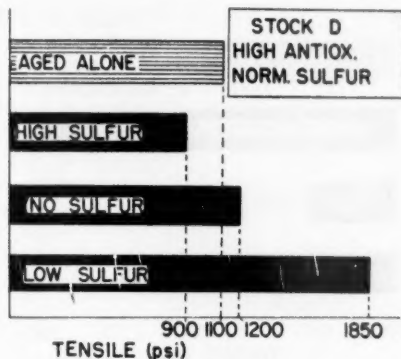


FIG. 3.—Comparison of aging characteristics of stock D. Aged alone and with stocks containing various amounts of sulfur.

less was left for protection of the parent stock. This performance suggests that antioxidant 5 is a more actively migrating material than the others in this test group.

MIGRATION OF OTHER MATERIALS

To show that materials other than antioxidants have migratory tendencies, the next to groups of stocks were aged individually and in various combinations. The first group of four stocks (Table III) consists of:

- D, high antioxidant, normal sulfur
- E, normal antioxidant, high sulfur
- F, normal antioxidant, no elementary sulfur
- G, normal antioxidant, low sulfur

By aging each of these stocks in a bomb with each of the others, it was shown that sulfur and probably accelerators migrate and that data obtained by community aging are completely unreliable. Test results produced by

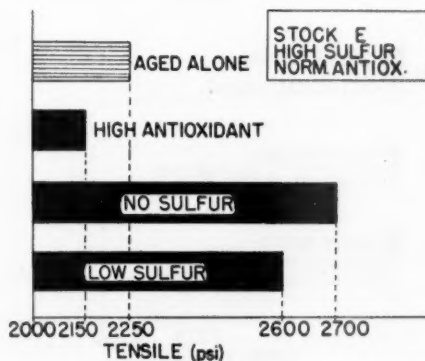


FIG. 4.—Comparison of aging characteristics of stock E. Aged alone and with stocks of different sulfur level and one with high antioxidant content.

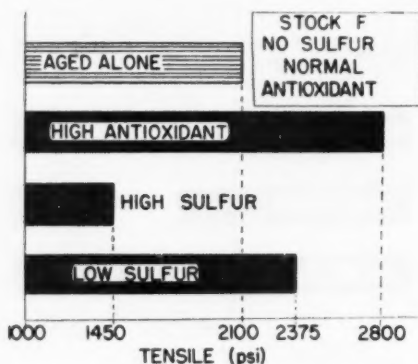


FIG. 5.—Comparison of aging characteristics of stock F. Aged alone and with stocks of different sulfur level and one with high antioxidant content.

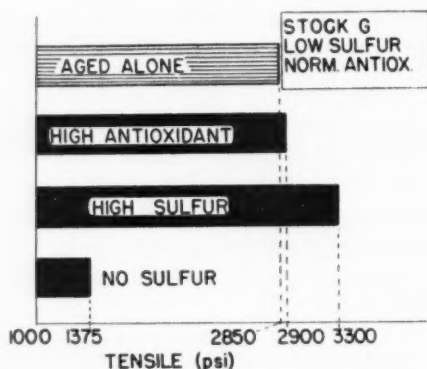


FIG. 6.—Comparison of aging characteristics of stock G. Aged alone and with stocks of different sulfur content and stock of high antioxidant content.

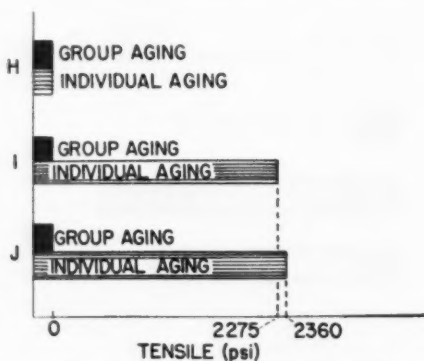


FIG. 7.—Effect of migration of cupric oleate on protected and unprotected stocks. Aged as a group and aged alone.

group aging methods are in error and the magnitude of the error is large enough to be significant.

Figure 3 amply demonstrates that materials other than antioxidants—namely, curatives—migrate and affect results. Stock D, containing high antioxidant and normal sulfur, was aged alone and with stocks containing various amounts of sulfur. The community aged samples produced a range of values from 900 to 1850 pounds per square inch, which is excessive for evaluation purposes. It is not contended that aging a normal sulfur stock with a low-sulfur stock will always increase the values, but such procedures will produce other than the true values.

Figure 4 shows that a stock containing low or no sulfur makes an artificial improvement in the apparent age resistance of a high-sulfur stock when the two

TABLE IV
EFFECT OF CUPRIC OLEATE MIGRATION

	H	I	J
Rubber	100	100	100
ZnO	5	5	5
Stearic acid	1	1	1
Sulfur	3	3	3
Benzothiazyl disulfide	1	1	1
Antioxidant 5 ^a	—	—	—
Antioxidant 7 ^b	—	1.5	1.5
Whiting	50	50	50
Cupric oleate	1	—	1
Tensile to break (lb. per square inch)			
Original	2950	2875	3325
Group aged		Melted	
Aged alone	Melted	2275	2360
Elongation to break (%)			
Original	760	790	810
Group aged		Melted	
Aged alone	Melted	750	735
Shore durometer values			
Original	38	38	35
Group aged		Melted	
Aged alone	Melted	37	38

^a Alkylated phenol sulfide.

^b N,N'-di-2-naphthyl-p-phenylenediamine.

are aged together. This shows that two stocks cannot be aged together in the same bomb, even when the only difference is in sulfur load.

Figures 5 and 6 further demonstrate the extent of variations in results which are brought about by the practice of community aging techniques. These variations are in some cases as large as 2000 pounds per square inch in aged tensile strength at break values.

With the work done to date, it is impossible to predict the effect of aging dissimilar stocks together.

Cupric oleate apparently migrates readily, and because of its severe action on natural rubber stocks, it is used to illustrate the extreme conditions that might be caused by material migration (Figure 7 and Table IV). Two of the last three stocks contain cupric oleate in combination with various quantities and types of antioxidants. All three stocks melted when aged as a group, but

when aged individually, stocks I and J showed a good retention of physical properties.

IDENTIFICATION OF MIGRATING MATERIALS

In the early experiments, the phenomenon being studied was assumed to be migration, although no confirming data were available. In order to confirm or deny the hypothesis of migration, qualitative chemical tests were run on samples after community aging in an attempt to detect the presence of a migrating material in a stock where originally none was present.

The presence of antioxidants was confirmed by means of spot test identification⁴. Stocks which originally contained no antioxidant showed a negative spot test, but after community aging gave positive tests for the presence of an antioxidant. This antioxidant was the same as that contained in one of the other stocks of the community group.

Quantitative sulfur determinations⁵ were performed to confirm the migration of sulfur from one stock to another. The results obtained were sufficient only to indicate that probably sulfur moves from one stock to another. The differences in percentage of sulfur obtained are small and, therefore, inconclusive. Additional precise testing is required.

The question of methods of avoiding migration arises. An attempt was made to prevent migration during oxygen-bomb aging by placing the different stocks in individual aluminum cans with loose-fitting lids within a single bomb. Data available but unreported show that aging in these containers is equivalent to group aging, without containers, and the results are significantly different from those obtained by individual aging. It is concluded, therefore, that the use of this device is not the solution to the migration problem.

The only adequate solution appears to be aging different stocks in separate bombs. All samples contained in a bomb at a given time must be of identical composition if results are to be reliable.

SUMMARY

It has been definitely established that various materials migrate and that the magnitude of the resulting error is significant. Migration takes place whenever unlike stocks are aged together in a bomb. The most reliable test conditions prevail when separate bombs are used for individual stocks. It is recommended that specifications for oxygen-bomb aging be changed. The change should specify the use of individual bombs.

ACKNOWLEDGMENT

The authors wish to express their appreciation to The Gates Rubber Co. for permission to publish this report, to Harold Thenhaus, who prepared the graphs, and to other members of the staff for constructive criticism in preparation of this manuscript.

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ESTIMATION OF THE TECHNOLOGICAL PROPERTIES OF RUBBER MIXTURES BY THEIR FLUIDITY *

F. I. GALPERINA

In our laboratory practice, plastometers of different constructions and operating on different principles are used for determining the plasticity of rubber and of rubber mixtures.

With all these instruments, the plasticity is measured at $70^{\circ} \pm 2^{\circ}$ C, and this makes impossible any estimation of the properties of rubber mixtures during the initial period of vulcanization, when they are heated to temperatures much exceeding 70° (up to 130° C and higher). Furthermore, the plasticity factor (according to Karrer) is the product of the softness and elasticity, which also are measured at 70° C. For this reason, plasticity gives no indication of the behavior of mixtures at vulcanization temperatures, particularly since there is no simple relation between the softness and elasticity of synthetic rubbers. In the production of shoes by hot vulcanization, it is essential to know the behavior of the rubber mixture in the initial period of vulcanization, i.e., during the period of fluidity, at temperatures from 130° to 140° C and higher, when molding.

An apparatus which we constructed, and which is shown in the figure, makes possible an estimation of the properties of rubber mixtures during vulcanization. It is composed of a plunger piston 1, set in a vessel 2, with oil heated to the desired temperature in order to create a uniform thermal medium. The piston is subjected to the pressure of a lever 3 with a movable weight.

The rubber test-specimen 4, which has been prepared on a die for the Williams plastometer, with a cross-sectional area of 2 sq. cm. and height of 5 or 10 mm., is heated to approximately 70° C, then is put in the cylindrical

TABLE I

Specimen no.	Height of column (mm.)	Experimental series
I	4.50	(1)
II	4.75	
III	4.50	
IV	4.50	
V	7.25	(2)
VI	7.25	
VII	7.00	
VIII	7.50	
IX	7.50	
X	7.50	
XI	10.00	(3)
XII	10.25	

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from *Legkaya Promyshlennost (Light Industry)*, No. 5, pages 44-45, May 1951.

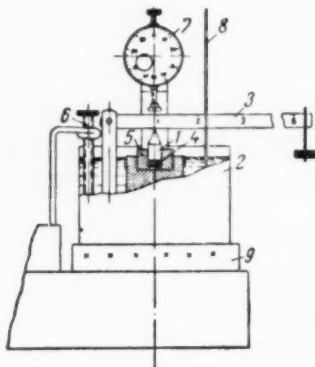


FIG. 1.—Apparatus for determining the properties of a rubber mixture during vulcanization. 1. Plunger piston. 2. Vessel containing oil. 3. Lever with weight. 4. Test-specimen. 5. Cylindrical matrix. 6. Counterweight. 7. Dial gauge. 8. Thermometer. 9. Electric heating plate.

matrix of the apparatus; the piston, with a central axial bore of 2 mm. diameter, is pressed on the specimen. Under the given pressure the specimen is vulcanized.

The molding properties of a mixture are characterized particularly by its fluidity, which is measured by the height (in mm.) of the column forced through the opening in the piston during the vulcanization process at the given pressure. The accuracy of this factor is shown by experimental data obtained in 1947. The experiments were performed with rubber mixture VI, of plasticity 29. Twelve specimens were tested at 150° C for a 6-minute vulcanization period; samples nos. 1 to 4 were tested at a pressure of 4.46 kg. per sq. cm., samples nos. 5 to 10 at 8.59 kg. per sq. cm., and samples nos. 11 and 12 at 13.3 kg. per sq. cm.; the height of the column for Experimental series (3) was equal to the subsequent values (see Table 1).

The error in making the first measurement with mean deviation $\sigma = 0.108$ was $\pm 3.57\%$, in making the second measurement, $\pm 3.51\%$, and in making the third measurement, $\pm 2.58\%$, with an accuracy of 0.997 for all the measurements. The experiments show the dependency of the fluidity factor on the age of the mixture; this is extremely important from a practical standpoint. The data below show the properties of mixture VI, tested at different time intervals after milling (Table 2).

TABLE II

Interval after milling	Softness		Elasticity		Plasticity		Fluidity	
Immediately after milling	0.373	100	0.927	100	0.346	100	7.22	100
4 hours after milling	0.358	91.0	0.871	94.0	0.295	85.0	5.47	76.0
24 hours after milling	0.260	70.0	0.812	88.0	0.211	61.0	4.14	57.0

In Table 2, two values are given for each property; at the left the absolute value, and on the right, the percentage; the values show the mean arithmetical values from the three measurements.

Experiments with mixture IV showed also that an increase of the time of milling greatly increases the fluidity in comparison with the other properties of the rubber mixture (see Table 3).

TABLE III

	Softness		Elasticity		Plasticity		Fluidity	
Before milling	0.358	100	0.863	100	0.308	100	3.60	100
After milling 10 min.	0.371	104	0.913	106	0.338	110	4.87	135
After milling 20 min.	0.373	104	0.923	107	0.314	111	5.90	164
After milling 30 min.	0.393	110	0.918	106	0.361	117	6.60	184

It is interesting to compare the data for plasticity and fluidity of mixture VI (before milling) with the same data for mixture VII (sponge rubber); this enables us to judge the importance of fluidity. Mixture VII had the following properties: softness, 0.534; elasticity, 0.743; plasticity, 0.395; fluidity, 21 (at a pressure of 6 kg. per sq. cm.). It is clear that the plasticity of mixture VII is 10 per cent greater than that of mixture VI, the softness 49 per cent greater, the fluidity of mixture VII is 5 or 6 times greater. Its behavior during the vulcanization process shows this strikingly.

Thus the fluidity of a rubber mixture is more significant than its plasticity for estimating its behavior in the initial period of vulcanization, when the mixture is subjected to compression and molding under the same conditions of temperature and pressure at which the measurements of fluidity are made in our apparatus.

This apparatus, because of its simplicity, can easily be assembled in the laboratory of any rubber footwear factory.

NONDESTRUCTIVE AGING TESTS FOR RUBBER *

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Accelerated aging tests have been used by the rubber industry for many years as a measure of product quality and for determining expected service life. Outdoor exposure tests have always shown poor correlation with accelerated tests because of the multiplicity of variables inherent in outdoor service conditions not met by an air oven or oxygen bomb methods.

A study of a large number of aged truck tires which had been tested in service showed that no significant correlation of physical properties could be established between tires that failed after a few hundred miles and those that finished the 10,000-mile test run. The data showing these comparisons are given in Table I.

TABLE I
SERVICE TESTS ON TRUCK TIRES

Physical property	Failure tires	Nonfailure tires
Tensile strength (av. % of original)	83.3	74.0
Elongation (av. % of original)	51.6	55.2
Hardness (av. points increase)	8.5	3
Av. mileage	3037	10,572
No. of tires	15	10

The conventional air-oven aging data for 7 days at 158° F and 70 hours at 212° F again show no correlation with natural weather aging (Table II).

TABLE II
AIR-OVEN AGING vs. WEATHER AGING OF TIRE TREAD STOCKS

Aging condition	Tensile strength (% retention)	Elongation (% retention)	Hardness (Points increase)
Air oven, 7 days at 158° F	107	76	6
Air oven, 70 hours at 212° F	92	53	10
Weather, 5 years	82	50	10

Typical aging curves for natural rubber specimens which were placed outdoors for three years in an unstressed position and indoors on a dark shelf show that the tensile and hardness may tend to increase at first and then decrease. The elongation loss is probably the most adequate criterion of aging. Data illustrating these physical property changes are shown in Figure 1.

The deteriorating influence of ozone and sunlight on rubber is shown by the aged tire in Figure 2. Tensile, elongation, and hardness at areas removed from the cracks indicate no serious losses of physical properties. Therefore it

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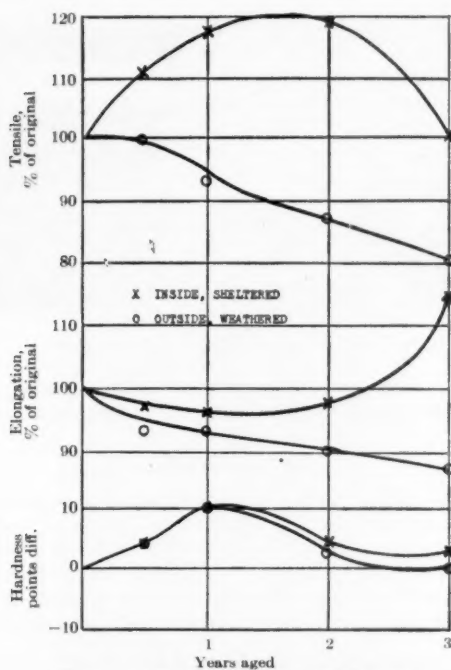


FIG. 1.—Changes in physical properties on aging.

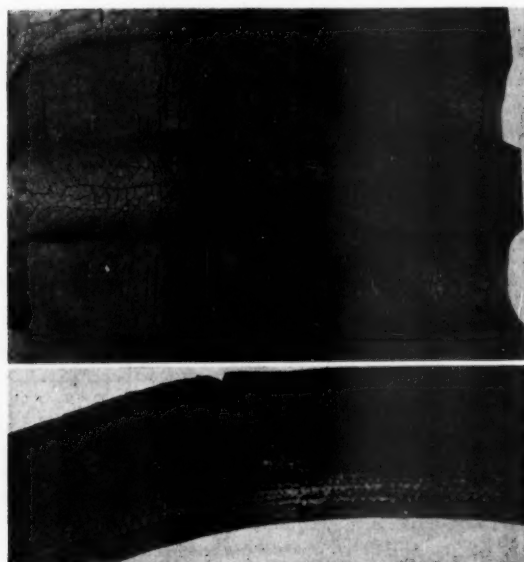


FIG. 2.—Effect of ozone and sunlight. Upper: Tread view. Lower: Section view.

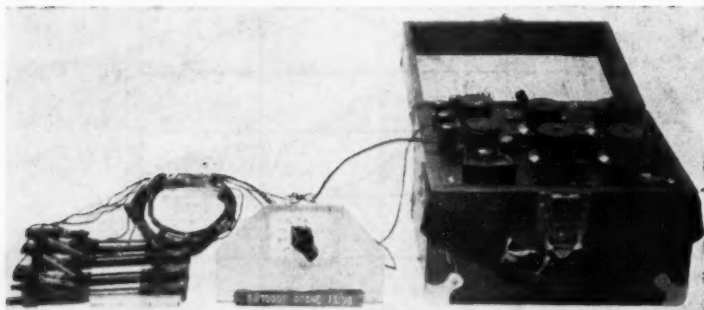


Fig. 3.—Apparatus for electrical resistivity method.

becomes imperative that an aging method be developed which takes into consideration the cracking produced by the action of ozone and sunlight.

TEST METHODS

A nondestructive rubber aging test should have good reproducibility; should be suitable for evaluating the effects of various aging media, such as heat, light, ozone, oxygen, and oils, either individually or collectively; should allow readings to be taken on the same specimen at progressive time intervals; and should express the result as a numerical quantity. Some progress in nondestructive aging tests has been made by Baxter, Morgan, and Roebuck¹ and by Tobolsky and coworkers².

ELECTRICAL RESISTIVITY METHOD

A GR-S compound containing 75 parts of acetylene carbon black per 100 parts of rubber and having a volume resistivity of 20 to 50 ohm-cm. was used for evaluating ozone cracking. T-50 specimens were cut both with and across the grain from a 0.080 inch sheet and stretched 25 per cent in metal clamps on a

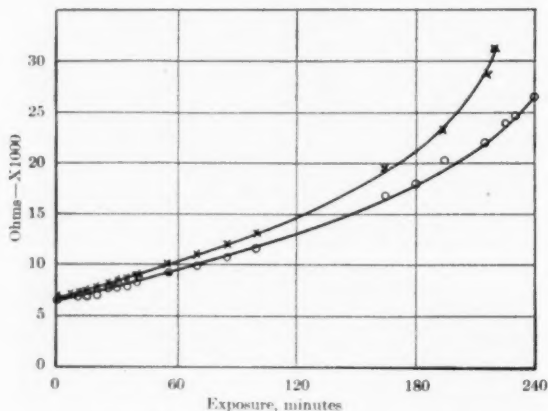


Fig. 4.—Effect of exposure to ozone concentration.

plastic insulating rod. The resistance of the rubber was determined, using a Wheatstone bridge.

The apparatus is shown in Figure 3. As the cracks develop in the specimen, the cross-sectional area is reduced and the volume resistivity increases. As many cracks are formed, the resistance reading is dependent on the crack producing the greatest reduction in area or the greatest penetration.

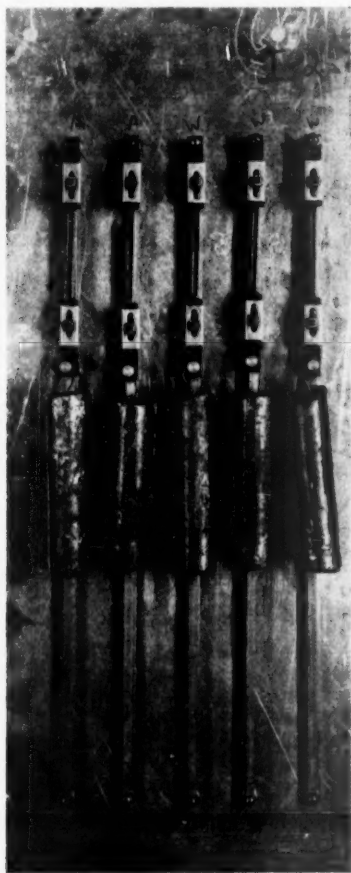


FIG. 5.—Test apparatus for reverse modulus method.

The data obtained from samples exposed to an ozone concentration of 0.015 per cent at 100° F are shown in Figure 4. The specimens were cracked sufficiently to break in the region of 30,000 ohms. The difference in the curves illustrates the effect of the grain, causing a higher resistance in one direction.

Tests made outdoors and proceeding under atmospheric ozone conditions gave similarly shaped curves, but were not reproducible. This may be attrib-

uted to variations in ozone concentration, temperature difference, and influence of moisture.

REVERSE MODULUS METHOD

The increase in elongation of a T-50 specimen caused by the application of a constant load to the stretched specimen at various time intervals was used to measure the amount of ozone cracking. The apparatus, shown in Figure 5, is a permanent-set apparatus mounted in a vertical position. The specimens are stretched 25 per cent and clamped at that extension. After exposure to ozone, the clamps are loosened, a 400-gram load is hung on the lower clamp, and the

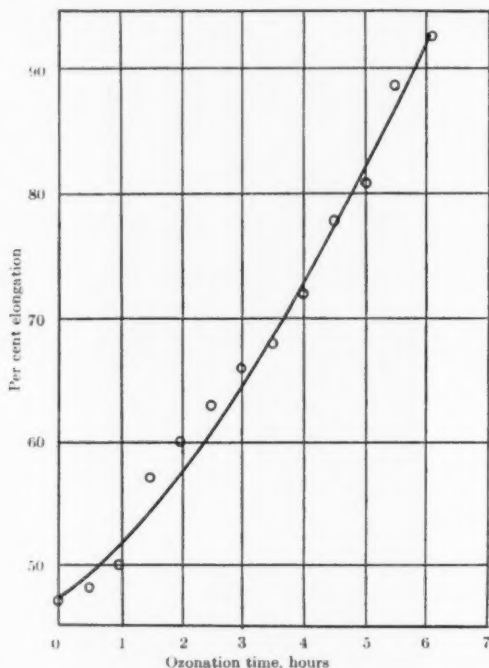


Fig. 6.—Ozone cracking.

resulting elongation is measured. Typical data for such a test are shown in Figure 6. As the cracks develop, the constant load causes an increase in elongation, thereby producing a measurable quantity.

STRAIN TEST METHOD

In view of the potentialities of the reverse modulus method, it was decided to investigate a more sensitive apparatus called the "strain tester for rubber". A picture of the apparatus is shown in Figure 7. The details of construction³ and the method of operation have been described⁴. The apparatus is well suited for determining the elongations cause by loadings at 100, 200, and 400 pounds per square inch. These elongations are high enough for good sensitivity

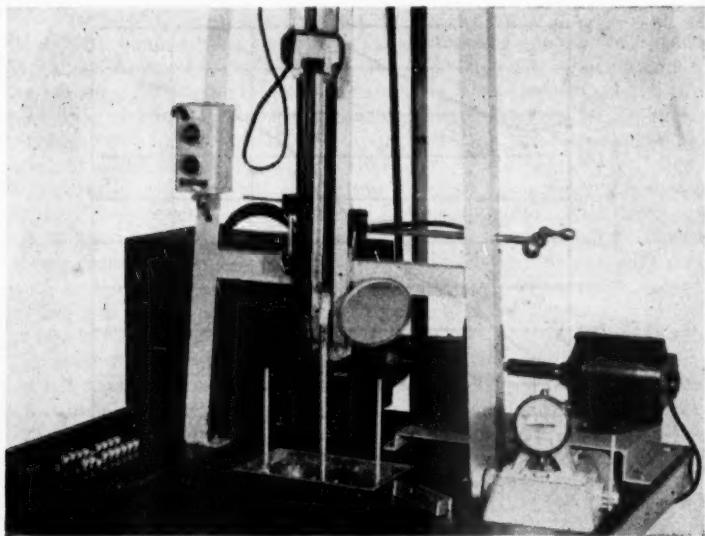


FIG. 7.—Strain tester.

and reproducibility, but not so high as to cause adverse effects such as permanent set or tearing. Measuring the elongation of rubber in the range 0 to 150 per cent, which includes all service usage, rather than the ultimate elongation at break, appears to be most desirable.

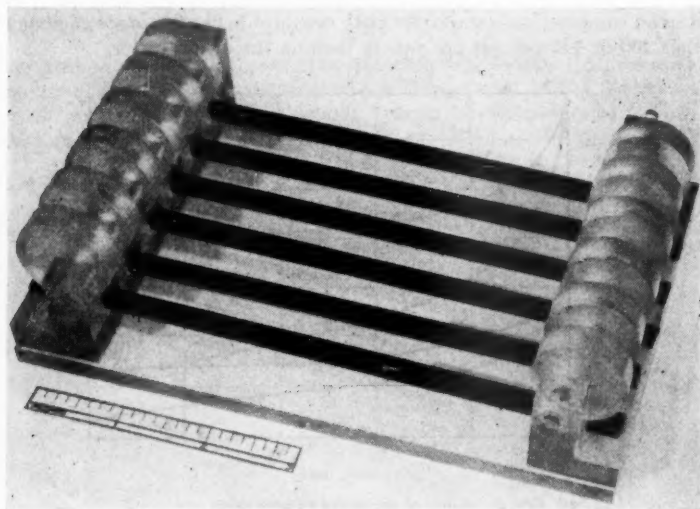


FIG. 8.—Stretch fixture.

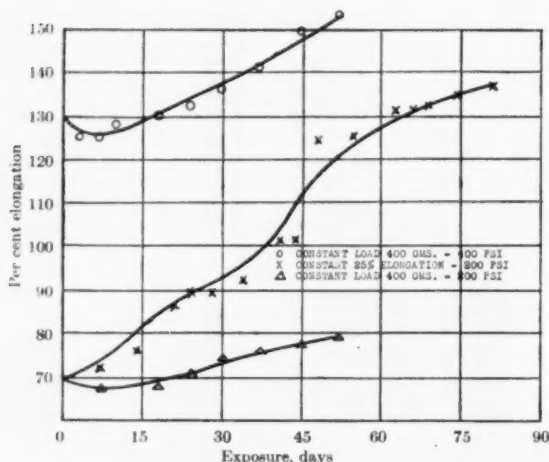


FIG. 9.—Effect of atmospheric ozone cracking.

The test specimens are $6 \times 0.25 \times 0.080$ -inch strips cut from standard pads. They are exposed either by hanging in the air oven for heat effects, or by being stretched 25 per cent in the plastic apparatus shown in Figure 8 and placed in an ozone cabinet. The stretch apparatus allows complete circulation of air or ozone around the specimen, and can be adjusted to any desired rate of extension merely by stretching the specimen and allowing the off-center wheel to serve as a wedge grip locking the specimen in position.

Figure 9 illustrates the type of information produced by the procedure described. In this case, the effect of atmospheric ozone cracking on a 90/10 GR-S tread composition is shown for both constant load and constant elongation at either 200 or 400 pounds per square inch on the strain tester.

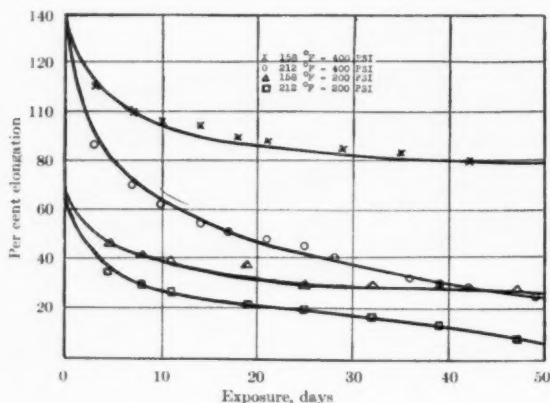


FIG. 10.—Effect of circulating air-oven aging tests.

The increase of slope of the constant elongation curve may be due to increased outdoor ozone concentrations. The decreased slope may indicate that cracking had developed to such a point that the stress was relieved somewhat and the cracking rate slowed down. Other tests have shown that the rate of ozone cracking is a function of the percentage elongation, not of the extent of the cracking. For this 90/10 GR-S compound, 18 per cent appeared to be the elongation at which cracks developed fastest.

The effects of conventional circulating air-oven aging tests are shown in Figure 10. These decreased elongations increased moduli with time are in contrast to the increased elongations observed in the ozone tests. Measurements were made at both 158° and 212° F, and at both 200 and 400 pounds per square inch loading. The tests, which were run up to sixty days, show that the greatest loss in elongation occurs during the first ten days.

The loss in elongation is probably the greatest factor in the failure of rubber items, as evidenced by both artificial and natural aging methods.

It is felt that the strain test method meets the requirements of a nondestructive rubber aging test, because it has good reproducibility, is suitable for evaluating the effects of various aging media, allows readings to be taken at progressive time intervals, and expresses the results as a numerical quantity.

SUMMARY

An improved laboratory method has been developed for evaluating the effects of aging. The test-specimens are subjected to definite loads or extensions at repeated intervals during exposure to the deteriorating influence of heat, light, air, and ozone. The degree of deterioration is evidenced by an elongation increase for specimens that become cracked and for a decrease in elongation for those that become heat-hardened. The test data are obtained on the same specimen at varying time intervals, are reproducible, and are measured in the low elongation range in which most rubber is used in service.

ACKNOWLEDGMENT

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- ⁴ Roth and Stiehler, *RUBBER CHEM. & TECHNOL.* **22**, 201 (1949).

IDENTIFICATION OF ACCELERATORS AND ANTIOXIDANTS IN VULCANIZATES BY INFRARED SPECTROSCOPY *

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INTRODUCTION

Reliable methods for the chemical analysis of vulcanizates have been available for many years, and standard methods have been published in a British Standard which has recently been revised¹, but these methods do not cover the identification of accelerators and antioxidants and no comprehensive scheme for this type of analysis has been published. The identification of accelerators and antioxidants in vulcanizates presents a difficult problem because of the small concentrations employed, the close chemical similarity of many of them, and the wide variety of substances used. Many chemical tests have been developed for their identification, but difficulties arise when they are applied to vulcanizates². On the whole these chemical tests are unsatisfactory, and it seems unlikely that a comprehensive chemical scheme can be devised for the identification of accelerators and antioxidants in vulcanizates. There are, however, several physico-chemical methods which can be used for such analyses.

The work of Proske³ has shown that accelerators in vulcanizates can be detected and estimated by the polarograph. The method is applicable to thiazoles, thiuram disulfides, and dithiocarbamates, but cannot be used with such accelerators as guanidines.

Chromatography has recently been applied to the problem with considerable success⁴. It has been shown that several accelerators give a characteristic chromatogram when the acetone extract of their vulcanizate is chromatographed on alumina, either alone or in the presence of cobalt oleate. In addition, antioxidants can be separated by chromatography from the rest of the acetone extract and can then be identified by color reactions. Although this method has been found in the R.A.B.R.M. laboratories to be very useful, there are serious difficulties in the way of developing a comprehensive scheme of analysis on this basis. For example, distinction between the various dithiocarbamate accelerators is difficult, and the method sometimes gives ambiguous results when applied to complex mixtures.

Ultraviolet spectroscopy has been applied to the detection of accelerators and their decomposition products in vulcanizates⁵, to the estimation of accelerators in masterbatches⁶, and to the quantitative estimation of antioxidants⁷. These applications suggest that ultraviolet spectroscopy should be a useful method for the identification of accelerators and antioxidants in vulcanizates.

Although infrared spectroscopy is well known to be a powerful tool for the identification of chemical compounds, there seems to be no recorded attempt to apply it to the present problem. Besides being able to distinguish between closely related compounds, infrared spectroscopy possesses the additional ad-

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vantage that, although not so sensitive as ultraviolet spectroscopy, only a few milligrams of a material is required for the recording of its spectrum, the material used being recoverable. It can thus be seen that infrared spectroscopy is a suitable tool for the identification of accelerators and antioxidants in vulcanizates, and the work reported represents an attempt to devise a comprehensive scheme for such analyses.

SPECTRA OF ACCELERATORS AND ANTIOXIDANTS

The spectra of a large number of accelerators and antioxidants have been recorded and a number of these are reproduced at the end of the paper. Accelerators and antioxidants which are single compounds were mostly commercial products which had been recrystallized from suitable solvents. Their melting points agreed with values given in the literature. The M.B.T. and M.B.T.S. were pure synthetic samples kindly supplied by Monsanto Chemicals, Ltd., and the P.P.D. and S.P.D. were similar samples kindly supplied by Robinson Brothers, Ltd.

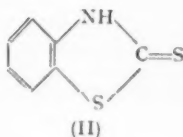
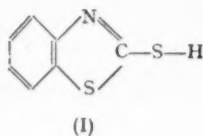
The compounds were measured as mulls in liquid paraffin, using a Grubb-Parsons single-beam spectrometer⁸ with rock salt optics. It can be seen that the compounds can be readily characterized by their spectra.

The dithiocarbamates and thiuram sulfides which have been measured show interesting strong absorptions in the region 1550–1400 cm^{-1} . Mulls in liquid paraffin show absorption bands at the following frequencies:

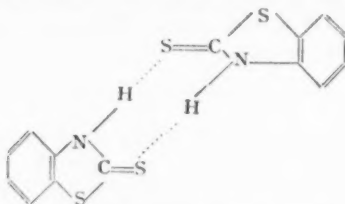
	cm^{-1}	cm^{-1}
Zinc pentamethylenedithiocarbamate (Z.P.D.)	1430	1480
Sodium pentamethylenedithiocarbamate (S.P.D.)	1420	1482
Nickel dibutyldithiocarbamate (N.B.C.)	1423	1500
Zinc dibutyldithiocarbamate	1425	1497
Zinc diethyldithiocarbamate (Z.D.C.)	1431	1502
Sodium diethyldithiocarbamate (S.D.C.)	1420	1482
Copper diethyldithiocarbamate	1435	1508
Zinc ethylphenyldithiocarbamate (Z.E.P.)	1420	1495
Tetraethylthiuram disulfide (T.E.T.)	1427	1502
Zinc dimethyldithiocarbamate	—	1515
Copper dimethyldithiocarbamate	—	1514
Tetramethylthiuram disulfide (T.M.T.)	—	1514
Tetramethylthiuram monosulfide	—	1514
Piperidine pentamethylenedithiocarbamate (P.P.D.)	1412	—
Diethylammonium diethyldithiocarbamate (D.D.C.N.)	1402	—

Compounds containing methyl groups usually exhibit absorption bands near 1460 and 1380 cm^{-1} . Since chloroform solutions of T.M.T. and zinc dimethyldithiocarbamate show strong bands near 1505 and 1380 cm^{-1} , but no absorption near 1460 cm^{-1} , the bands of the methyl compounds near 1515 cm^{-1} are probably due to deformations of the methyl groups. The interpretation of the other bands is less clear, and a greater variety of compounds will have to be examined before definite assignments can be made.

Two structures are possible for M.B.T., the thiol form (I) and the thiocarbonyl form (II):



Ultraviolet spectra show that M.B.T. has the thiocarbonyl structure in solutions in alcohol, benzene, and chloroform, and it has been suggested that M.B.T. exists as the hydrogen-bonded thiocarbonyl form in the solid⁸:



The spectrum of solid M.B.T. shows no band near 2500 cm^{-1} , a frequency characteristic of S—H groups, suggesting that it does not have the thiol form. The alternative thiocarbonyl form, however, should show a band due to a N—H stretching vibration. The spectrum shows no band attributable to such a vibration, but this could well be caused by the suggested hydrogen-bonding in the solid, since hydrogen-bonding always lowers the frequency of X—H stretchings and frequently broadens their absorptions. If hydrogen bonding occurred the N—H absorption might be obscured by the intense absorption due to C—H groups at lower frequencies.

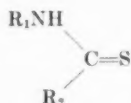
The frequencies of absorption of solid M.B.T. and related molecules in the region $1600\text{--}1400\text{ cm}^{-1}$ are shown below:

	cm^{-1}	cm^{-1}	cm^{-1}
2-Mercaptobenzothiazole (M.B.T.)	1594	1495	1425
Benzothiazolyl disulfide (M.B.T.S.)	1590	—	1430
2-Benzothiazolyl <i>N'</i> -cyclohexyl sulfenamide (C.B.S.)	—	—	1431
Zinc salt of M.B.T. (Zenite)	—	—	—
Copper salt of M.B.T.	—	—	—

M.B.T. is characterized by the strong band at 1495 cm^{-1} where the other compounds show no detectable absorption. Chloroform solutions of M.B.T. show the same band near 1495 cm^{-1} , while no band is detectable in solutions of C.B.S. and M.B.T.S. Since C.B.S. and M.B.T.S. are derivatives of the thiol form of M.B.T. while M.B.T. is known to have the thiocarbonyl structure in solutions, it seems probable that the difference observed at 1495 cm^{-1} is due to this difference in structure.

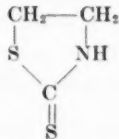
Many compounds containing a substituted aromatic ring absorb near 1500 cm^{-1} , and it is possible that the 1495 cm^{-1} band is due to a vibration of the *ortho*-disubstituted ring. There are other reasons for believing that the thiocarbonyl form should absorb strongly near 1500 cm^{-1} , however.

Randall¹⁰ has found a strong band between 1615 cm^{-1} and 1445 cm^{-1} in compounds of the type:



This band has been called the thioureide ion band and is shown by the com-

pound 2-thiothiazolidone:



This compound has been shown to have the thiocarbonyl form and to have a strong thioureide ion band at 1515 cm^{-1} . Since the thiocarbonyl form of M.B.T. has a similar structure, the 1495 cm^{-1} band in solutions of M.B.T. can be interpreted in a similar way.

The 1495 cm^{-1} band of the solid can also be interpreted in the same way, and the infrared spectrum is compatible with the proposed thiocarbonyl structure for solid M.B.T.

The 1495 cm^{-1} band of solid M.B.T. could also be interpreted in terms of the thiol form, however. Crystallization is known to affect the intensities of some bands, and the 1495 cm^{-1} band can be interpreted as being due to a vibration of the aromatic ring of the thiol form, the difference between M.B.T. and M.B.T.S. and C.B.S. being due to the different intermolecular forces in the crystals.

METHOD OF ANALYSIS

It is impossible to identify accelerators and antioxidants by measuring the spectrum of the vulcanizate because of the small proportions present. In general it is also impossible to identify these substances by measuring the spectrum of the acetone extract, since this is a complex mixture and some of its components absorb strongly in the infrared. For these reasons the accelerators and antioxidants were separated chromatographically from other components of the extract and were then identified spectroscopically.

The chromatographic method used was based on that described by Bellamy, Lawrie, and Press⁴ and is as follows. Ten grams of vulcanizate was acetone-extracted, and the dried extract was dissolved in warm benzene. After cooling, the solution was filtered and the filtrate allowed to pass down a column of B.D.H. analytical grade alumina. The column was then washed successively with about 200 cc. each of benzene, 0.25 alcohol—99.75 benzene, 1 alcohol—99 benzene, 5 alcohol—95 benzene and absolute alcohol, the figures indicating parts by volume. Fractions were collected by observing the colored rings on the column and the color of the eluate. The eluted fractions were then evaporated and the infrared spectra of the residues measured.

Bellamy, Lawrie, and Press have shown that paraffin wax, mineral oil, free sulfur, and stearic acid do not interfere with the separation of accelerators and antioxidants. The pine tar used by these authors gave only one eluted fraction, suggesting that it would cause no interference. The pine tar used in the present work, however, gave more fractions. In addition to the ring eluted by a 5 alcohol—95 benzene mixture, which was observed previously, benzene eluted a yellow fraction which was not detected as a ring on the column. A 1 alcohol—99 benzene mixture eluted a yellow ring, and absolute alcohol washed out a dark brown fraction. It seems possible, therefore, that pine tar may interfere in certain cases with the separations of accelerators and antioxidants.

In addition to compounding ingredients, two fractions which originate in the pale crepe are eluted from the column. Fraction I was eluted by benzene and

is a yellow oily liquid of unknown constitution. Fraction II, whose composition is also unknown, was eluted as a yellow ring by a 1 alcohol—99 benzene mixture.

IDENTIFICATION OF ACCELERATORS IN VULCANIZATES

Since many accelerators give rise to decomposition and reaction products during vulcanization, it is necessary to establish the nature of these products before unknown vulcanizates can be characterized. The following series of vulcanizates were examined for this purpose:

Base mix: pale crepe 100, zinc oxide 5, stearic acid 1; plus M.B.T. 0.5, sulfur 2.5; M.B.T.S. 0.5, sulfur 2.5; C.B.S. 0.8, sulfur 3; Z.D.C. 0.4, sulfur 2; T.E.T. 0.5, sulfur 1.05; T.M.T. 0.4, sulfur 2; T.M.T. 2; P.P.D. 0.5, sulfur 2; D.D.C.N. 0.35, sulfur 2; Z.I.X. 0.75, sulfur 2; D.P.G. 0.5, sulfur 3; D.O.T.G. 0.5, sulfur 3; butylaldehyde-aniline (Vulcafor BA) 0.7, sulfur 2.5; methylene-*p*-toluidine (Vulcafor MT) 0.5, sulfur 3.5.

The compounds were vulcanized to an approximate optimum.

THIAZOLES

The ultraviolet spectroscopic work of Dufraisse and Houpillart¹¹ has shown that rubbers containing M.B.T. or M.B.T.S. before vulcanization contain both M.B.T. and M.B.T.S. after vulcanization; other workers¹² have suggested that M.B.T. is converted into its zinc salt during vulcanization. In the present work only M.B.T. was detected, in the alcohol eluate from the column. However, any M.B.T.S. or zinc salt formed during vulcanization would be detected as M.B.T., since under the conditions used both these compounds are converted into M.B.T. on the column.

The accelerator from the M.B.T.S. vulcanizate was also detected in the alcohol eluate as M.B.T., and the present method thus does not enable vulcanizates compounded respectively with M.B.T. and M.B.T.S. to be distinguished. The work of Dufraisse and Houpillart, however, suggests that this would not be possible even if an adsorbent were found which did not convert M.B.T.S. into M.B.T.

The chromatograms of the M.B.T. and M.B.T.S. vulcanizates were simple and contained no highly colored rings. The chromatogram of the C.B.S. vulcanizate on the other hand was more complex and contained highly colored rings. However, the only fraction which could definitely be characterized as a decomposition product of the accelerator was the alcohol eluate, which contained M.B.T. The most interesting of the other fractions was a pink zone eluted by a 1 alcohol—99 benzene mixture. Its spectrum showed that it was mainly fraction II from the pale crepe, but the absorption bands of medium intensity at 751 and 691 cm^{-1} could not be attributed to this fraction. Although the cause of these bands is unknown, the fact that they are absent in the spectra of the corresponding fractions from the M.B.T. and M.B.T.S. vulcanizates suggests that they may be used to characterize C.B.S. vulcanizates, though this may not be possible with complicated vulcanizates which may contain other substances that absorb at these frequencies.

The zinc salt of M.B.T. finds use in the Zenite accelerators and can also be used as an antioxidant¹³. As stated above, it is converted into M.B.T. on an alumina column, and the M.B.T. from vulcanizates containing Zenite can readily be detected.

DITHIOCARBAMATES AND THIURAMS

The Z.D.C. in the vulcanizate could not be detected by the method outlined above. It could, however, be detected by chromatographing the extract after adding a benzene solution of cobalt oleate. The green Z.D.C.—cobalt oleate complex so formed gave rise to two green zones on the column. One of these could not be eluted, while the other was rapidly eluted by benzene. The spectrum of this latter fraction was largely that of the accelerator, apart from the band at 1550 cm^{-1} which was due to the cobalt oleate. All dithiocarbamates that have been examined gave a similar fraction, and this method is thus useful in identifying small quantities of dithiocarbamates.

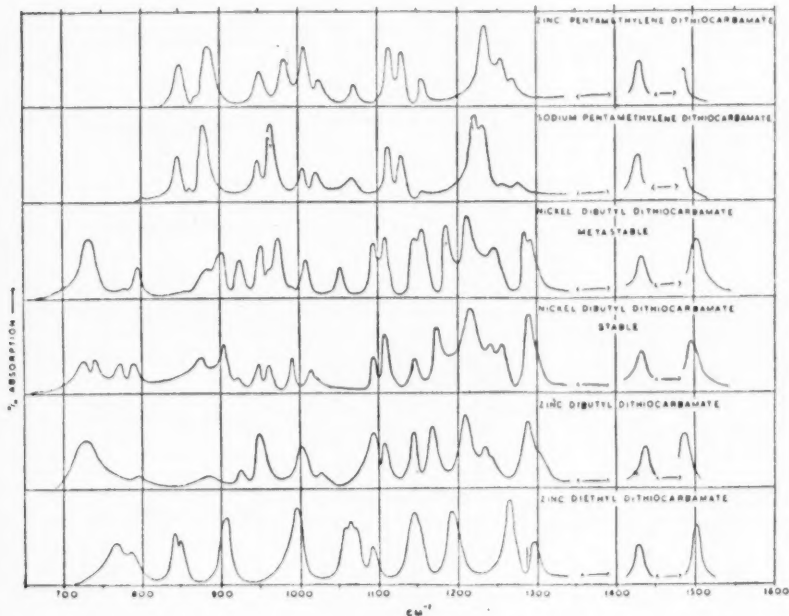


Fig. 1.

Other vulcanizates accelerated by Z.D.C. were examined, and the Z.D.C. was detected in the 5 alcohol—95 benzene eluate. It is presumed that these vulcanizates contained more residual Z.D.C. Vulcanizates containing Z.P.D. behave in the same way as Z.D.C. vulcanizates, and the Z.P.D. can be identified in the 5 alcohol—95 benzene eluate unless only small quantities are present.

The chromatogram of a benzene solution of D.D.C.N. with cobalt oleate differs from those of other dithiocarbamates that have been examined. Benzene elutes a broad green zone and 1 alcohol—99 benzene mixture elutes a brown ring. A 5 alcohol—95 benzene mixture elutes a second green ring, and alcohol elutes a greenish-brown solution, leaving a green ring at the top of the column. D.D.C.N. can be identified spectroscopically in the benzene and 5 alcohol—95 benzene fractions.

In addition to the pale crepe vulcanizate, latex vulcanizates accelerated by D.D.C.N. have been examined, cobalt oleate being added before chromatographing. With all the vulcanizates, vulcanized at 100° C, the green complex of Z.D.C. was identified in the benzene eluate. Some undecomposed D.D.C.N. was present, however, as a 5 alcohol—95 benzene mixture eluted a second green ring and D.D.C.N. was identified in this fraction. Unless all the D.D.C.N. has decomposed, this second green ring provides a useful way of distinguishing vulcanizates accelerated by D.D.C.N. or Z.D.C.

Although several vulcanizates accelerated by P.P.D. and vulcanized at 100° C have been examined, no fraction has been found which would enable the vulcanizates to be identified. Since it has been reported that zinc oxide and

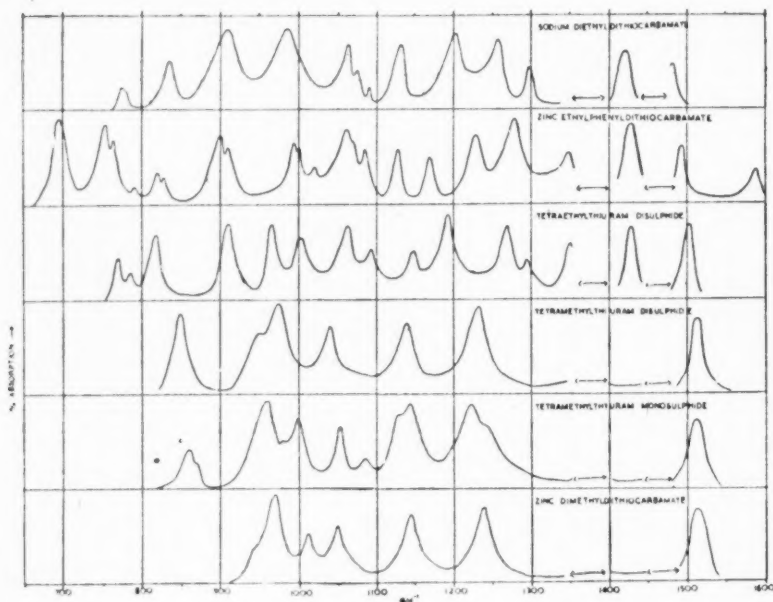


Fig. 2.

P.P.D. form Z.P.D. at room temperature¹⁴, it was anticipated that the accelerator would be present as Z.P.D. after vulcanization. However, neither Z.P.D. nor unchanged P.P.D. was detected. A vulcanizate prepared from latex gave an alcohol fraction the spectrum of which suggested that it was derived from the accelerator. Vulcanizates prepared from pale crepe, however, did not give a similar fraction. It seems that P.P.D. undergoes extensive decomposition during vulcanization at 100° C, though the nature of this decomposition is not clear. The results obtained with the latex vulcanizates suggest that it may be possible to characterize some P.P.D. vulcanizates, and further work is being done on this subject.

Although not an accelerator, nickel dibutylthiocarbamate is conveniently discussed with the dithiocarbamates. It finds some use as a protection against

ozone and flex cracking¹⁵ and can be used to protect Neoprene vulcanizates from discoloration by light. The chromatogram from a vulcanizate containing N.B.C. showed a broad green ring which was washed off the column by benzene. The spectrum of this fraction differed from that of N.B.C. recrystallized from alcohol, but on standing for a few days its spectrum changed into that of the recrystallized N.B.C. Further work has shown that it is possible to obtain both forms by recrystallization from alcohol and that one form is metastable, passing into the other at room temperature. N.B.C. obtained by evaporation of a benzene solution always has the spectrum of the metastable form, though it may change on standing into that of the stable form.

Dufraisse and Jarrijon¹⁶ have shown that during vulcanization in presence of zinc oxide T.M.T. is converted into zinc dimethyldithiocarbamate. In the

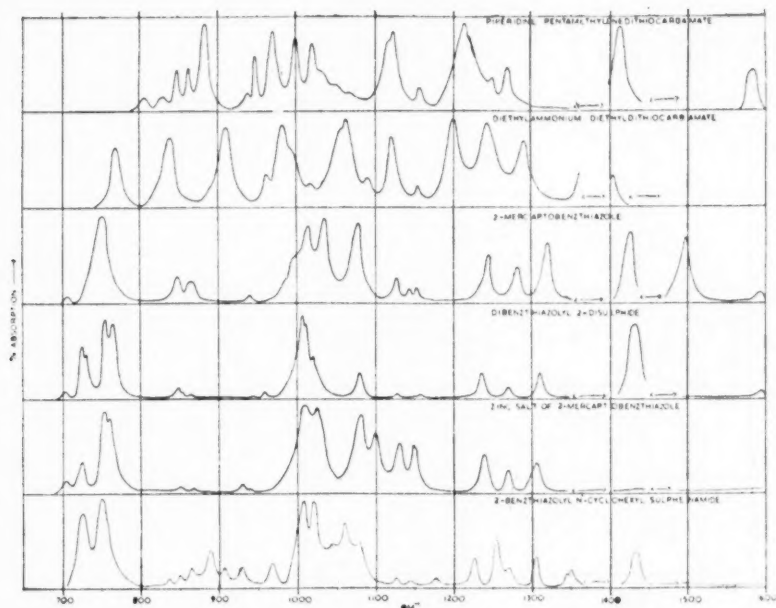


Fig. 3.

present work zinc dimethyldithiocarbamate was detected in the 5 alcohol—95 benzene eluate of the sulfurless T.M.T. vulcanizate. The dithiocarbamate was detected also in the benzene eluate of a cobalt oleate chromatogram from the sulfur vulcanizate accelerated with T.M.T. No further characteristic fraction has been found which would enable vulcanizates accelerated by T.M.T. or zinc dimethyldithiocarbamate to be distinguished.

T.E.T. behaves in the same way as T.M.T. and was detected as Z.D.C. after vulcanization.

T.E.T. and T.M.T. can be identified as such in unvulcanized mixings. They react with the acetone during extraction, however, giving derivatives which seem to contain carbonyl groups. These derivatives are eluted from the



FIG. 4.

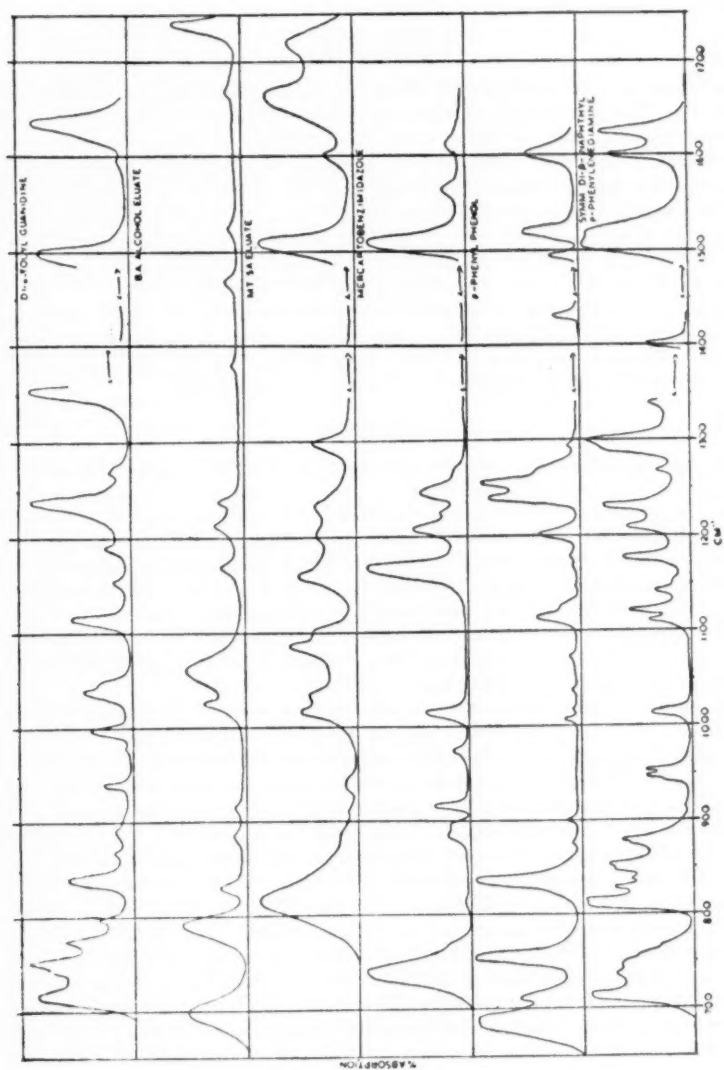


FIG. 5.

column as brown rings by a 0.25 alcohol—99.75 benzene mixture. The derivatives can be identified spectroscopically, since they show absorption bands of both the accelerator and acetone. If the extraction is carried out with a different solvent, the accelerators are eluted by a 5 alcohol—95 benzene mixture.

XANTHATES

Vulcanizates accelerated by Z.I.X. have been prepared from both latex and pale crepe. The compounds were vulcanized at 100° C and room temperature. The only fraction observed which could be attributed to the accelerator was a green fraction eluted by benzene from a cobalt oleate chromatogram. The amount of this green complex, however, was too small for it to be identified spectroscopically. The results show that Z.I.X. undergoes decomposition during vulcanization at 100° C and at room temperature, no recognizable decomposition products being formed. Latex vulcanizates accelerated by S.P.X. and prepared at 100° C and room temperature gave similar results.

Z.I.X. can, however, be identified in unvulcanized compounds by chromatographing the acetone extract with cobalt oleate. Two green zones are eluted from the column by benzene, and the cobalt oleate complex can be identified spectroscopically. A third green ring remains on the column.

GUANIDINES

The fate of D.P.G. during vulcanization has been investigated by several workers. Wistinghausen¹⁷ developed a method for estimating unchanged D.P.G. by forming its picrate, and thus followed the consumption of D.P.G. during vulcanization. Humphrey¹⁸ reinvestigated this method and found that part of the D.P.G. was not extracted by acetone but could be extracted by acetone containing a little hydrochloric acid. The complex chromatograms observed by Bellamy, Lawrie, and Press⁴ suggest that decomposition products of D.P.G. are extracted from the vulcanizate by acetone. In contrast to this work, however, Dufraisse and Houpillart¹¹ detected no unchanged D.P.G. or decomposition products in the extract.

The present work confirms that substantial amounts of substances derived from D.P.G. are extracted, since several fractions showed strong absorption bands near 750 cm^{-1} and 690 cm^{-1} , frequencies characteristic of monosubstituted benzene rings. Although no fraction had the same spectrum as crystalline D.P.G., the fraction eluted by alcohol had a similar spectrum, and it is suitable for the characterization of D.P.G. vulcanizates. The fractions eluted by a 5 alcohol—95 benzene mixture were combined, and a picrate was prepared from them which melted 3° C lower than D.P.G. picrate, and had a spectrum almost identical with that of the pure picrate. The fraction eluted by alcohol gave a smaller amount of a similar picrate. The chemical identity of this fraction is uncertain, however. The fraction may have contained some of the preceding fraction and, in addition, the fact that its spectrum was not completely identical with that of crystalline D.P.G. does not prove conclusively that it is not D.P.G. The fraction was not crystalline and it is well known that crystallization can markedly affect the spectrum of a substance¹⁹.

The extract of the vulcanizate accelerated by D.O.T.G. gave a complex chromatogram containing several colored rings. A 5 alcohol—95 benzene mixture eluted two brown rings and following these a yellow solution. This solution contained unchanged D.O.T.G. and is the most suitable fraction with which to characterize vulcanizates accelerated by D.O.T.G. Absolute alcohol

eluted a brown resinous material, the spectrum of which showed it to be a decomposition product of the accelerator.

ALDEHYDEAMINE ACCELERATORS

Two vulcanizates accelerated by aldehydeamine accelerators have been examined. The accelerators were a reaction product of butylaldehyde and aniline and a reaction product of formaldehyde and paratoluidine. The commercial products used were Vulcafor B.A. and M.T., respectively.

The chromatogram of the B.A. vulcanizate contained several colored rings, the most characteristic being a bright crimson ring eluted by a 0.25 alcohol—99.75 benzene mixture. Its spectrum showed, however, that the ring consisted largely of a fraction from the crepe rubber, the color presumably being due to a small amount of contaminant. Although absolute alcohol did not elute a ring, it emerged from the column as a brown solution. The spectrum of this fraction shows that it is derived from the accelerator.

The vulcanizate accelerated by M.T. gave a chromatogram containing brown and yellow rings and a pink ring. A 5 alcohol—95 benzene mixture eluted a brown ring which fluoresced in ultraviolet light. The spectrum of this fraction differs from that of the original accelerator, but indicates that the fraction was derived from the accelerator. In particular, the intense band at 815 cm^{-1} is probably due to a vibration of the aromatic ring of the accelerator.

IDENTIFICATION OF ANTIOXIDANTS IN VULCANIZATES

With the exception of Flectol-H, all the antioxidants examined by Bellamy, Lawrie, and Press were only weakly adsorbed by alumina and were eluted from the column by benzene. The present work has shown however, that this is not a general property of antioxidants, many of them requiring more polar solvents for elution. The vulcanizates used contained 0.5 parts antioxidant per 100 of rubber and the columns were viewed in ultraviolet light to assist separation of the antioxidants.

Phenyl β -naphthylamine was completely eluted from the column by benzene and was readily identified in this fraction spectroscopically. Its fluorescence provided a sensitive way of following its elution.

The chromatogram of the vulcanizate containing *sym*-di- β -naphthyl-*p*-phenylenediamine (Agerite White) was similar to that described by Bellamy, Lawrie, and Press with the exception that under the conditions used in the present work a 1 alcohol—99 benzene mixture was required for complete elution of the antioxidant, though it was eluted slowly by a 0.25 alcohol—99.75 benzene mixture. The intense spectrum of the antioxidant allowed it to be detected without interference from the rubber fraction which is eluted from the column by the same solvent mixture.

p-Phenylphenol (Parazone) is more strongly adsorbed by alumina than the previous two antioxidants, and also differs from them in not being fluorescent on the column. The chromatogram was simple and the *p*-phenylphenol was present as a yellow ring, which passed slowly down the column with a 1 alcohol—99 benzene mixture and was finally eluted by a 5 alcohol—95 benzene mixture. It was readily identified spectroscopically in this fraction.

The vulcanizate containing Nonox-NS (a phenol-aldehyde-amine reaction product) gave a chromatogram which seemed simple in visible light, but contained several fluorescent zones when viewed in ultraviolet light. The antioxidant was found to be present in all fractions except the benzene fraction

containing free sulfur, though much of it was eluted as a brown ring by a 1 alcohol—99 benzene mixture. All fractions containing antioxidant gave a spectrum similar to that of the original antioxidant.

The vulcanizate containing Flectol-H (an acetone-aniline condensation product) gave a chromatogram similar to that described by Bellamy, Lawrie, and Press. Although benzene eluted some antioxidant, the bulk was eluted by a 1 alcohol—99 benzene mixture and was easily identified in this fraction by its spectrum.

The vulcanizate containing Nonox-HF, which is a mixture, gave a chromatogram containing four colored rings. Although elution of the antioxidant was completed with a 1 alcohol—99 benzene mixture, the bulk of it was eluted by benzene. The spectrum of the latter fraction was not identical with that of the original antioxidant, but was sufficiently similar for characterization of the antioxidant. The fraction eluted by a 0.25 alcohol—99.75 benzene mixture had a spectrum quite different from that of the original antioxidant, and is probably a second minor component of the mixture.

Mercaptobenzimidazole is one of the "deactivators" described by Le Bras²⁰. Vulcanizates containing this substance have been examined, and it was found possible to identify it in the fraction eluted by a 5 alcohol—95 benzene mixture. Indirect evidence suggests that this substance is present as the zinc salt in vulcanizates containing zinc oxide²¹. The fact that it was detected as the thiol is not in disagreement with this view, however, as the zinc salt is converted into the thiol on the column.

IDENTIFICATION OF ACCELERATORS IN VULCANIZATES CONTAINING ANTIOXIDANTS

It has been shown in the previous section that some antioxidants are completely eluted from the column only by polar solvent mixtures. Vulcanizates containing 0.5 parts each of antioxidant and accelerator have been examined, therefore, to demonstrate that it is usually possible to identify accelerators in the presence of antioxidants by the present method.

Two vulcanizates accelerated by M.B.T. and containing *p*-phenylphenol and Nonox-NS, respectively, have been examined. No difficulty was experienced in identifying the accelerator in the fractions eluted by absolute alcohol. Although there was evidence of some Nonox-NS in this fraction, the amount present was too small to cause interference.

A vulcanizate containing *p*-phenylphenol and D.P.G. has also been successfully analyzed. The parazone was cleanly separated from the characteristic D.P.G. alcohol eluate and both ingredients were easily characterized spectroscopically.

A vulcanizate containing phenyl- β -naphthylamine and Z.D.C. has also been examined. The vulcanizate contained 0.5 parts of Z.D.C., and the accelerator was identified in the 5 alcohol—95 benzene eluate. This may not be possible, however, when smaller quantities of Z.D.C. are present. In this case it has been shown that the Z.D.C. can be identified by combining all the fractions except the benzene fraction and rechromatographing them with cobalt oleate. The green complex of Z.D.C. can then be identified in the benzene eluate.

These results, together with those reported by Bellamy, Lawrie, and Press, suggest that in most cases it will be possible to separate antioxidants and accelerators in such a way that they do not interfere with one another's identification.

LIMITATIONS OF METHOD

The method of analysis outlined above has been in use in the R.A.B.R.M. laboratories for some time and has been successfully applied to vulcanizates of unknown composition. Examples which can be quoted are the successful analysis of a vulcanizate containing *sym.*-di- β -naphthyl-*p*-phenylenediamine, M.B.T., and D.P.G. and the identification of a butylaldehyde-aniline accelerator in a vulcanizate containing pine tar. The method has also been used to detect the T.E.T. present in Neoprene-GN and the Z.D.C. to which it gives rise when Neoprene-GN—natural rubber mixtures are vulcanized.

Although experience has shown the method to be valuable, it has limitations. It has been mentioned above, for example, that the identification of accelerators may be more difficult when pine tar is present. Pine tar is unlikely to interfere with the identification of accelerators which are single compounds, but its presence undoubtedly complicates the identification of accelerators such as the aldehyde amines, which are complicated mixtures, despite the fact that one successful example of this type of analysis has been described above. The problem of the detection of aldehyde-amine accelerators is difficult and is likely to be even more difficult in the presence of antioxidants which are themselves mixtures. Further work will be required on this subject before the limits of the method can be precisely defined.

Although the method outlined offers a reasonable solution to the problem of the qualitative analysis of vulcanizates for accelerators and antioxidants, it is unlikely that it can ever be made quantitative. In the first place infrared spectroscopy suffers from the disadvantage of a lack of suitable solvents for accelerators. Secondly, even where this does not apply, it is essential to separate the ingredient chromatographically. This involves the use of large quantities of solvent which then have to be evaporated and the residue dissolved in a small quantity, say 10 cc., of a suitable solvent.

In addition to the chemical methods which exist for the estimation of individual accelerators and antioxidants, the most promising methods seem to be polarography and ultraviolet spectroscopy. The latter method has the advantage over infrared spectroscopy of being more sensitive to the accelerators and antioxidants.

IDENTIFICATION OF BLOOMS

The spectra of accelerators and antioxidants which have been measured are also of use in the identification of blooms. If a bloom can be removed by scraping or by a solvent, measurement of its spectrum provides a rapid method for its identification. In addition to applications to commercial vulcanizates, this method has been used to show the differences in composition between the wax added to a rubber mix and the bloom which it produces on the vulcanized rubber²².

METHOD OF ANALYSIS OF UNKNOWN VULCANIZATES

The method used for the analysis of unknown vulcanizates is as follows. Ten grams of the vulcanizate is acetone-extracted by the conventional method and the extract is evaporated to dryness. The residue is dissolved in warm benzene, the solution is allowed to cool, and is then filtered. Warm benzene is necessary to ensure solution of substances, such as M.B.T., which are difficult to dissolve. The benzene solution is passed down an alumina column (B.D.H. analytical grade) and the column is washed with approximately 200 cc. each of benzene, 0.25 alcohol—99.75 benzene, 1 alcohol—99 benzene, 5 alcohol—95

benzene mixtures, and absolute alcohol, the figures indicating parts by volume. The column is viewed in ultraviolet as well as visible light, and suitable fractions are collected by observing the passage of colored rings down the column and the color of the eluate. The fractions are then evaporated to dryness and the spectra of the residues are measured, the material used being recovered.

All the fractions with the exception of the benzene fractions are then dissolved in benzene and the solutions combined. A benzene solution of cobalt oleate is then added and the mixture is passed down a second alumina column. The column is washed with benzene and, if a green fraction is eluted, the eluate is evaporated to dryness and the spectrum of the residue measured. This second stage is necessary to identify any dithiocarbamates or xanthates which are not detected in the first stage.

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DETERMINATION OF FREE SULFUR IN VULCANIZED RUBBER MIXTURES *

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Numerous papers on the determination of free sulfur in rubber mixtures have been published. Most of these are in the older literature, and they offer various methods for determining free sulfur. In principle the methods can be divided into two general groups. The procedures described in the first and larger group involve preliminary acetone extraction before the actual determination of the free sulfur¹, whereas the methods comprising the second group, which include only two different procedures, do not involve acetone extraction². Of these two methods, only that of Oldham, Baker, and Craytor³ has found widespread acceptance.

THE EFFECT OF COLD ACETONE EXTRACTION IN COMPARISON WITH HOT ACETONE EXTRACTION

The utility of all procedures in the first group mentioned above was suddenly questioned when Lindsly⁴ published the results of experiments with cold acetone extraction. These results supposedly proved that, during the hot extraction in a Soxhlet apparatus, which was in such general use at the time, vulcanization reactions take place and that these lead during the extraction to a decrease of free sulfur originally present in the sample. This decrease was found to take place not only in mixtures vulcanized with ultra-accelerators, which is quite understandable, but particularly in mixtures vulcanized with mercaptobenzothiazole as the accelerator.

Lindsly arrived at these results with the use of an extraction apparatus, specially constructed by him, which was so designed that the sample to be extracted came in contact only with cold acetone. By comparative experiments, Lindsly was able to prove definitely that a hot-extracted sample contained, after extraction by acetone, a higher percentage of combined sulfur than that of a corresponding cold-extracted sample.

We have recently studied this subject in an experimental way, for it did not seem that it had, since the work of Lindsly, been approached from any new viewpoint.

EXPERIMENTAL PART

For the cold extraction of rubber, an apparatus was constructed, which in principle was similar to that of Lindsly. With this apparatus, a number of vulcanizates which differed greatly in composition were analyzed for their percentages of combined sulfur after 24 hours' hot extraction and after 24 hours' cold extraction. The analyses are recorded in Table 1.

The data in Table 1 show that the combined sulfur content after hot extraction is, in general, lower than after cold extraction.

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from *Fresenius' Zeitschrift für Analytische Chemie*, Vol. 133, No. 4, pages 274-282 (1951).

TABLE 1
COMBINED SULFUR REMAINING IN VULCANIZATES AFTER HOT EXTRACTION
AND AFTER COLD EXTRACTION WITH ACETONE

Sample	After hot extraction	After cold extraction
1	1.16	1.21
2	1.51	1.53
3	1.44	1.70
4	0.71	0.86
5	1.24	1.44
6	1.13	1.33
7	2.91	3.20

The method of determining the combined sulfur contents was to decompose the sample by aqueous perchloric acid and nitric acid in the presence of magnesium oxide, and then to determine the sulfate as barium sulfate. In some cases comparative analyses were made by a method to be described later, whereby the sulfate was titrated photometrically, as will be described in the present work in connection with the determination of acetone-soluble sulfur.

Lindsly carried out his experiments with two specially prepared unvulcanized rubber mixtures, and since he gave the exact compositions of these mixtures, it was possible to produce these mixtures in the work to be described. In our opinion, the results obtained differed from those of Lindsly because of the different effects of cold extraction and hot extraction. This confirmed our expectation that quite different results from those of Lindsly would be obtained.

Table 2 gives the actual analyses, which show that vulcanization reactions during extraction with hot extraction cannot explain the results obtained.

Having found that an unvulcanized sample contained, after extraction by cold acetone, a higher percentage of combined sulfur than the percentage in the same mixture after extraction by hot acetone, the time of cold extraction was standardized at 48 hours. In order to be assured of optimum conditions for the thorough extraction of unvulcanized mixtures, the weighed samples were sheeted out thin on a laboratory mill, covered while still on the rolls with a piece of filter paper, and rolled up in the latter. In this way, there was no chance of the sample forming a coherent mass during the extraction. When extracted under these conditions, none of the samples contained, after hot extraction, more sulfur than did the corresponding samples after cold extraction.

TABLE 2
EFFECT OF EXTRACTION BY COLD ACETONE IN COMPARISON
WITH EXTRACTION BY HOT ACETONE⁴

Analysis of two unvulcanized rubber mixtures

Recipe and analyses	Mixture I	Mixture II
Natural rubber	100	100
Sulfur	3	0.5
Mercaptobenzothiazole	0.5	3
Stearic acid	1	1
Zinc oxide	5	5
Total sulfur, elemental and in the accelerator	2.91	1.51
Combined sulfur remaining after extraction of the raw mixture by hot acetone	0.10	0.13
Corresponding values of Lindsly ⁴	1.09	0.44
Combined sulfur remaining after extraction of the raw mixture by cold acetone	0.27	0.18
Corresponding values of Lindsly	0.05	0.19

Certainly under these conditions, where the samples were not heated, it is not correct to speak of "combined" sulfur in the true meaning of the term, for the sulfur which is still present after the cold extraction can hardly be regarded as combined, but rather should be regarded as adsorbed by the sample itself and by the filter paper.

COMPARISON OF THE RESULTS OBTAINED ON THE ONE HAND
BY THE STANDARD PROCEDURE AND, ON THE OTHER HAND,
BY THE METHOD OF OLDHAM, BAKER, AND CRAYTOR

The method developed by Oldham, Baker, and Craytor has, as already mentioned, been widely accepted, and has, in our opinion, various merits. In principle, the sample, in the form of a thin sheet, is heated for two hours in boiling 5 per cent aqueous sodium sulfite solution. The free sulfur reacts with the sodium sulfite to form sodium thiosulfate, and this is determined iodometrically. However, the procedure gives low values in comparison with those obtained by the standard procedure, *i.e.*, extraction by acetone, oxidation of the extract by nitric acid and bromine, and gravimetric determination of the sulfate.

Table 3 records a number of comparative analyses.

TABLE 3
FREE SULFUR FOUND IN VULCANIZATES AS DETERMINED BY THE METHOD
OF OLDHAM, BAKER, AND CRAYTOR, AND BY THE STANDARD
PROCEDURE INVOLVING ACETONE EXTRACTION
(Values in percentage)

Sample no.	By the method of Oldham, Baker, and Craytor	By the standard method with acetone extraction
1	0.52	0.84
2	0.04	0.13
3	0.04	0.11
4	0.35	0.56
5	2.05	2.13
6	5.82	6.50
7	1.00	1.00
8	0.46	0.46
9	0.85	1.08
10	0.21	0.56
11	0.20	0.80

Why the method of Oldham, Baker, and Craytor gives lower values than does the standard methods cannot be answered on the basis of any experimental facts. The most important question, however, is which of the two methods should be recommended for general use. First of all, it has been found that results obtained by the sodium sulfite method can be reproduced very accurately. In addition, the method is much more rapid than is the standard method, and in industrial rubber laboratories, this can be of great importance, for many times the rubber technologist must know the free sulfur content of a sample in a very short time. In most of these cases, errors in curing are in question, and in such instances a normally and correctly cured sample of the same rubber mixture is almost always available for a comparative analysis. Here the rubber technologist needs to know only relative values of the free sulfur, though naturally he wishes these to be as precise as possible. Under these conditions the sodium sulfite method is, according to the experience of the present author, of outstanding value.

Returning, however, to the low results which are obtained by the method, as exemplified by the data in Table 3, a negative error generally results from the fact that only part of the sulfur in sulfur-bearing accelerators reacts with the sodium sulfite, whereas with the standard acetone extraction method all of the sulfur in the accelerators appears in the results. Thus by the sodium sulfite method, only the sulfur of the thiol group in mercaptobenzothiazole reacts with sodium sulfite, whereas by the standard method the sulfur in the ring as well is determined.

The treatment with cadmium acetate recommended by Oldham, Baker, and Craytor was not utilized in the analyses which are discussed here⁵.

The differences in the results by the two methods in the case of Samples 2 and 3 in Table 3 are with the greatest probability attributable to the sulfur-bearing accelerators which they contained, but in general this is not a satisfactory explanation of the differences in the results which were obtained by the two different methods.

The generally negative errors of the sodium sulfite method can be demonstrated by a model analysis of the unheated standard rubber mixture of Lindsly (see Table 2). Table 4 gives the analytical results.

TABLE 4
RESULTS OBTAINED BY THE OLDHAM, BAKER, AND CRAYTOR METHOD OF
ANALYSIS OF THE UNHEATED STANDARD MIXTURE OF LINDSLY
(Values in percentage)

Free sulfur	Mixture I	Mixture II
Elemental and in the accelerator	2.82	0.97
Found by the method of Oldham, Baker, and Craytor	2.63	0.67

If the argument of Lindsly is followed here, the thought occurs that during the two-hour treatment of the sample in sodium sulfite solution at about 100° C, some vulcanization takes place. In any case this possibility seems more reasonable than it would for an acetone extraction at 57° C, if the difference in the surrounding medium is disregarded.

It was also found experimentally that samples which had been treated by the sodium sulfite method still contained in all cases small percentages of acetone-soluble sulfur. However, these residual contents of free sulfur were nowhere nearly great enough to explain the differences in the values obtained by the standard method and by the sodium sulfite method. On the other hand, it should be emphasized that the differences between the values of the unvulcanized mixtures (see Table 4) were of the same order of magnitude as the differences for the mixtures after vulcanization (see Table 3). This fact can hardly be said to be evidence in favor of vulcanization taking place during the sodium sulfite treatment in the method of Oldham, Baker, and Craytor.

In a further series of experiments, several samples were treated in the usual way with sodium sulfite solution, but this time in a vacuum, whereby the solution boiled at 40° C. After 14 hours of such treatment in vacuo, the analyses gave values of the free sulfur which averaged 80 per cent of the values obtained by the sodium sulfite treatment under normal operating conditions.

DISCUSSION

Finally we wish to take up a problem in terminology which was also mentioned by Lindsly. He called attention to the fact that the ASTM Standards

classify free sulfur⁶ as the "sulfur which is soluble in acetone". This is certainly not correct, for, according to this definition, the sulfur would be tacitly understood to include all sulfur in acetone-soluble sulfur-containing compounds. Yet the 1949 edition of the Standards still contains this definition. In this connection it is of interest to note that this same ASTM Standards includes the sodium sulfite method of Oldham, Baker, and Craytor as an "alternate method".

So, in view of the comparative results shown in Table 3, the analytical chemist finds himself in the unusual position that he can report either of two different methods as correct, provided only that he specifies which of the methods he has used in his analyses. As an analytical chemist, the present author can only regret to be obliged once more to make such an admission, but there seems to be no alternative.

Returning now to the problem of what method is to be recommended for general use in determining free sulfur in rubber mixtures, the answer must be to some extent an evasive one. The method of Oldham, Baker, and Craytor is at least as useful in the industrial laboratory as the method which involves acetone extraction, but which method should be employed must be decided in each particular case on the basis of the conditions and purpose involved, and the final choice of method will depend on how the rubber technologist intends to utilize the results. Since, however, a gravimetric determination of small amounts of acetone-soluble sulfur is sometimes difficult, we shall describe another volumetric method which makes possible, with the aid of a photoelectric colorimeter, the determination, with satisfactory precision, of small amounts of acetone-soluble sulfur.

DETERMINATION OF SMALL QUANTITIES OF ACETONE-SOLUBLE SULFUR

Small quantities of sulfate can be titrated photometrically to the point of maximum turbidity. In this case the ammeter of the colorimeter functions as the indicator of the end point. A Lange colorimeter is used. The solution to be analyzed is placed in the right cell of the apparatus. During the titration a precipitate is formed, and this is kept uniformly dispersed by means of a mechanically driven glass stirrer. The needle of the ammeter continues to move uniformly during the titration, but it suddenly becomes stationary when the stoichiometrically necessary quantity of barium chloride has been added. From this point on, no more precipitate is formed, and at this same moment the stopcock of the burette is closed.

Standard solution.—0.02 N barium chloride solution, which has been standardized gravimetrically.

Apparatus.—Lange colorimeter or any other apparatus which serves a similar purpose. Mechanical stirrer.

Procedure.—The acetone extract is oxidized in the conventional manner by nitric acid and bromine in the presence of a moderate quantity of magnesium oxide (0.3–0.5 gram). The dry residue is treated with concentrated hydrochloric acid, evaporated, dissolved in hot distilled water containing a few drops of dilute hydrochloric acid, neutralized with N sodium hydroxide solution (until the hydroxide precipitate just dissolves), cooled, the clear solution transferred quantitatively to a 100-cc. measuring flask, and the flask filled to the mark.

A measured quantity of this solution is placed in a 100-cc. flask, 30 cc. of ethanol is added, the solution is made up to 90–100 cc. with hot distilled water, brought to 40° C, the flask is placed in a colorimeter, a stirrer and burette are

assembled in position, and the titration is carried out, slowly and continuously, until the needle of the ammeter becomes stationary, i.e., until no more precipitate is formed.

It was found of advantage to use blue-green filters. A negative correction factors of 0.3 cc. was adopted, because this much is overtitrated before one is assured that the ammeter needle actually has become stationary. The operation is best carried out with a semimicroburette (total capacity 25 cc. and graduated in 0.05 cc. units). The optimum operating range is the consumption of 5-10 cc. of 0.02 *N* barium chloride solution.

Table 5 gives a few analytical results.

TALBE 5
RESULTS OBTAINED BY PHOTOMETRIC TITRATION
(Values in percentage)

Sample no.	Acetone-soluble sulfur by the standard method	Acetone-soluble sulfur by photometric titration
1	0.82	0.74
2	0.52	0.55
3	2.13	2.16
4	0.11	0.09

By this method very small quantities of acetone-soluble sulfur can be determined with satisfactory precision under conditions where a gravimetric determination by the standard procedure is difficult and inexact.

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DETERMINATION OF TOTAL SULFUR IN VULCANIZED RUBBER MIXTURES *

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Ordinarily in the analysis of vulcanized rubber mixtures, the sulfur is oxidized to sulfate, and the latter is then determined gravimetrically as barium sulfate. Many ways have been proposed for improving this gravimetric determination of sulfate¹, and there has been a real need for such improvements; first of all, because barium sulfate crystals are very fine, so that the precipitate must be allowed to stand a long time for it to change to a form which can be filtered with reasonable ease. The proposals which have been aimed at the most rapid possible crystal growth or coagulation effects² have been prompted by the customary demands of industry for rapidity of operation.

In the second place, a number of proposals have had as their aim the elimination of the influence of certain cations³, whose presence has a disturbing effect on the determination, either by precipitation or by masking the reaction.

The disturbing effects of cations are practically uncontrollable because positive and negative errors result concurrently. Chromium and iron form soluble complex sulfates and thus lead to negative errors (see Table I). On the other hand, barium sulfate carries down iron and chromium ions during its precipitation and occludes them so that they cannot be washed out of the precipitate. This leads to positive errors. Alkali salts have this same disturbing effect⁴. The possibilities of calcium salts causing errors have been described by Goehring and Darge⁵.

Rapid volumetric procedures for the determination of sulfate⁶ are reliable only in the absence of disturbing cations.

The sum total of the disturbing effects of alkali salts, ferrous salts, ferric salts, and tervalent chromium salts naturally depends on the concentrations of these salts relative to the concentration of the sulfate present. The disturbing effect of alkali salts is of concern when the oxidative decomposition is carried out by sodium peroxide in a Parr bomb and the sulfur is then precipitated as barium sulfate⁴.

Disturbances by iron salts and chromium salts are particularly notable in the analysis of mixtures which contain iron oxide or chromic oxide pigments. Experience has also proved that many types of clay and whiting which are used by the rubber industry contain, by analysis, considerable amounts of iron. If such a filler is present in high volume in a rubber mixture, this iron is included in the sulfur determination, and therefore it would seem advisable in such cases to eliminate the effect it has on an analysis by the artifice which is proposed in the present work.

Separation of iron and chromium in the hydroxide form leads to completely erroneous results (see Table I), while methods for the more nearly complete

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TABLE I
EFFECTS OF CHROMIUM OXIDE PIGMENT ON THE DETERMINATION OF TOTAL
SULFUR IN A VULCANIZED RUBBER MIXTURE ACCORDING TO THE
PARTICULAR PROCEDURE EMPLOYED FOR THE ANALYSIS
(Theoretical value = 1.53 per cent)

Procedure	Per cent sulfur	Per cent error
Precipitation as hydroxide	1.07	-30
	1.23	-20
Tervalent chromium	1.54	+ 0.65
	1.32	-13.7
	1.22	-20.3
	1.55	+ 1.3
	1.47	- 3.9
Masking with tannin	1.54	+ 0.65
	1.51	- 1.3
	1.51	- 1.3
	1.47	- 3.9
	1.54	+ 0.65
	1.54	+ 0.65
Masking with acetic acid	1.74	+13.7
	1.73	+13.
	1.73	+13.
Wofatit-benzidine	1.52	- 0.65
	1.53	0
	1.53	0

separation of hydroxides are much too time-consuming, as shown by Goehring and Darge⁵.

For a long time there has been a very good possibility of avoiding the difficulties encountered as a result of the disturbing effects of foreign cations in sulfate analyses. Samuelson⁷ and also Goehring and Darge⁵ have already described the use of ion exchange synthetic resins in sulfate analysis, and the present author himself has made use of this means of eliminating completely any disturbing cations from his experimental solutions. For this purpose a Wofatit-KS exchange reagent of the Bayerwerk Leverkusen has been employed with success. After the exchange reagent has passed into solution, the sulfate is precipitated as benzidine sulfate and is titrated with aqueous sodium hydroxide⁸. The conditions to be described are applicable to practically all methods for the determination of sulfate, and in particular to those which are sensitive to the disturbing effects of cations. In spite of the opinion of Thomson⁹, we regard the benzidine method as very useful.

OPERATING METHOD

REAGENTS

Nitric acid (density 1.42).

Perchloric acid (60-70 per cent).

Bromine.

Sodium hydroxide (0.1 N solution).

Sodium hydroxide (1 N solution).

Benzidine solution.—Twenty grams of benzidine is stirred and warmed with 400 cc. of water and 25 cc. of hydrochloric acid (density 1.19) until a clear solution is obtained. The solution is then filtered and made up to one liter.

Hydrazine hydrochloride.

Wofatil-KS No. 22. Column 17 cm. high (see Figure 1)¹⁰. ϕ 2.8 cm. Approximately 52 grams of dry resin is needed for the purpose. The exchange system is treated with 7.5 per cent hydrochloric acid and then washed with distilled water until the wash liquor no longer gives a positive test for chlorides.

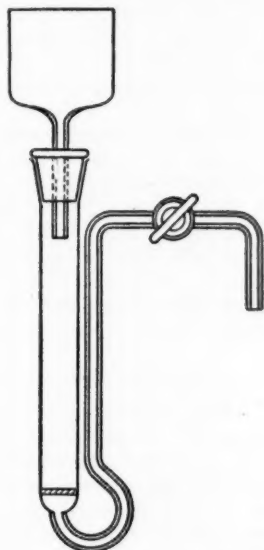


FIG. 1.—Simple glass apparatus for experiments with ion exchange agents.

ANALYTICAL PROCEDURE

Grind 1–1.5 grams of the sample of vulcanized rubber on a tightly closed mill, add the macerated rubber, 0.2 gram of magnesium oxide, 50 cc. of nitric acid (density 1.42), and 3–4 cc. of bromine successively to a wide-mouth Erlenmeyer flask (250 cc. capacity), allow the mixture to stand 30 minutes, heat slowly to the boiling point, evaporate almost to dryness on a sand bath, add 20–30 cc. of nitric acid, then 8 cc. of perchloric acid, and heat to vigorous boiling on a sand bath. When the acid has been reduced to one-half its original volume, add 10 cc. more of perchloric acid, and evaporate to dryness, provided that no dark colored residue is still to be seen. If, however, such a residue still appears, heat the mixture again with perchloric acid. With carbon black mixtures, this decomposition usually does not require more than one and one-half hours. To the light salt crust, add about 100 cc. of water and 1 cc. of hydrochloric acid (density 1.16), heat the mixture to the boiling point, filter hot, wash thoroughly with warm water, approximately neutralize the solution with 1 *N* sodium hydroxide, dissolve any hydroxide which may be precipitated by adding just enough 1 *N* hydrochloric acid; pour the solution, whose temperature must be in the range of 20–30° C, at the rate of 30–40 cc. per minute through the already prepared exchange column, and allow to flow into a 500-cc. measuring flask.

With mixtures which contain iron oxide or chromium oxide pigments, add 0.3–0.4 gram of solid hydrazine hydrochloride to the solution and boil the mixture for 5 minutes before it is passed through the resin. After cooling, the exchange system is next treated as follows. Wash the column twice, each time with about 100 cc. of water at 30–40° C, and fill the flask to the 500-cc. mark. With a pipette remove twice, 200 cc. each time, and, after having neutralized each part with 1 *N* sodium hydroxide (with phenolphthalein as indicator), add 10 cc. of benzidine solution dropwise to each of the two parts. The temperature of the solutions must be below 20° C.

Allow the mixture containing the precipitate to stand for 15 minutes, lower the temperature to 10° C, filter through a double blue ribbon filter into a Buchner funnel under not too high a vacuum, wash the residue twice, each time with 10 cc. of distilled water, place the filter paper with its precipitate in an Erlenmeyer flask having a ground-glass stopper, add 100 cc. of water, warm to 60–70° C, agitate for one minute, open the flask, rinse the stopper and inner walls of the flask with water, rotate the flask rapidly, titrate with 0.1 *N* sodium hydroxide and phenolphthalein until the solution is rose colored, then heat the contents of the flask to the boiling point, and titrate to the end point. From the amount of standard sodium hydroxide consumed, calculate the percentage of sulfur in the rubber mixture.

SUMMARY

A method is described, which, by means of a resin ion-exchange agent, makes possible the elimination of the disturbing effects of foreign cations, particularly iron and chromium, in the determination of the total sulfur in vulcanized rubber mixtures. By this procedure, rapid volumetric methods for determining sulfate, even in the analysis of mixtures containing iron oxide or chromium oxide pigments, can be utilized. The procedure involves precipitation of the sulfate by benzidine and determination by titration with aqueous sodium hydroxide. The method is more rapid and more reliable than ordinary gravimetric methods involving precipitation of barium sulfate.

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IMPROVEMENTS IN ACCURACY OF HARDNESS TESTING *

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INTRODUCTION

Committee ISO/TC/45 (Rubber) of the International Organization for Standardization has recommended, as the preferred form of hardness test, that based on indentation of the rubber by a rigid ball under specified conditions of loading. At the 1949 meeting of the Committee, it was agreed to adopt the following features in this hardness test:

- (1) use of a presser foot surrounding the indenter and resting on the rubber;
- (2) application of a small ("zero") load to the indenter before taking the zero reading;
- (3) application of gentle vibration to the instrument, if this includes parts (*e.g.*, a dial micrometer gauge) liable to develop slight friction;
- (4) lubrication of the rubber surface with talc.

Evidence was submitted at the meeting to show that all these features improve the accuracy of the test. The purpose of this paper is to record and discuss this evidence.

The experiments described in the section on "Vibration and Lubrication" were organized by the British Delegation to ISO/TC/45 in accordance with the decision at the 1948 meeting; acknowledgment is made of the help given by the following laboratories, which took part in the experiments: The British Rubber Producers' Research Association, Dunlop Rubber Co., Ltd., Greengate and Irwell Rubber Co., Ltd., Imperial Chemical Industries, Ltd., and the Bragg Laboratory, Naval Ordnance Inspection Dept.

Except where otherwise stated, all hardness tests were made with a 3/32-inch diameter ball, and the result is expressed as depth of indentation in mm/100.

PRESSER FOOT AND ZERO LOAD

CAUSES OF ERROR IN HARDNESS TESTS

It is essential to begin with a clear idea of the likely causes of error in measuring the indentation produced by the ball and the reasons that have led to the adoption of a zero load and (or) a presser foot.

In all hardness gauges the indentation is measured by the movement of the plunger carrying the indenting ball. This movement must be measured from a zero position, and the fixing of this zero position has been the cause of most of the difficulties hitherto encountered.

The ideal zero position would be that where the ball is just touching the rubber surface. Unfortunately this is impracticable because the ball cannot be

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made definitely to touch the rubber without exerting a slight force on it, and this produces an indentation of indefinite depth, so that the "zero" will be a false one. Experience has proved that taking the point of first contact between ball and rubber as the zero is unsatisfactory. Two alternative solutions of the difficulty have accordingly been devised:

Zero Load.—A definite known load (small compared with the main indenting load) is applied to the ball, and its position under this load taken as the "zero".

Presser Foot.—An annular foot, surrounding the indenter, rests on the rubber surface; the depth of indentation is measured relative to the plane of this foot, on the assumption (which is not necessarily true) that when the ball is just touching the rubber its tip is in this plane.

Either of these methods would be satisfactory for test-pieces with perfectly flat and parallel faces and having lateral dimensions considerably greater than the thickness. Unfortunately few test-pieces conform to these requirements, since even those intended to have flat parallel faces usually depart slightly from this ideal. Even a slight departure can be serious; with a rubber of hardness 90 degrees (B.S. or Shore, equivalent to B.S. hardness number 20) a curvature or local surface depression of only 0.05 mm., and thus not evident to the eye, would cause a 25 per cent error in the measured indentation. Although flat parallel-faced test-pieces are always specified in standard hardness test procedures, this is an unattainable ideal, and it is thus essential that the method should give accurate indentation measurements on test-pieces that do not conform to these requirements.

Errors due to the lateral dimensions of the rubber not being sufficiently larger than the thickness arise with small manufactured articles rather than laboratory test pieces.

We must now consider how departure from the ideal test-piece shape affects indentation measurements obtained by the zero-load and presser foot methods respectively.

ERRORS IN ZERO-LOAD METHOD

When a zero load is used without a presser foot, the measuring gauge has a fixed position relative to the base surface on which the test-piece rests; movement of the indenter is thus measured relative to this base surface. It is thus assumed that the zero position, that is, the upper surface of the rubber, remains fixed relative to the base surface. Inaccurate results will, therefore, arise if the upper surface of the rubber as a whole is depressed when the main indenting load is applied, because the amount of this depression will be added to the measured indentation. This can occur in the following cases:

- (1) If the under surface of the rubber is slightly concave.
- (2) If, in superimposing two or more thicknesses, air-gaps are left between them, owing to their not being quite flat.
- (3) In the case of relatively small test-pieces (say, not above 1 inch square or diameter) if the test-piece has a thickness comparable with or greater than its lateral dimensions, so that it compresses bodily under the main load.

The error in cases (1) and (2) can be as large as the thickness of the air gap under or within the test-piece. The hardness readings in Table I were obtained on plied-up test-pieces from smooth molded sheets 0.10 inch thick; the loads

TABLE 1
EFFECT OF PLIED-UP TEST-PIECES ON INDENTATION (MM./100)

Number of plies.....		1	2	3	4
Pure-gum rubber	With foot	75	97	105	108
	Without foot	80	103	114	120
	Difference	5	6	9	12
Tire tread rubber	With foot	59	62	64	64
	Without foot	62	67	70	83
	Difference	3	5	6	19

were 30 and 565 grams, and the foot was 1.6 cm. diameter pressed on to the rubber by a load of 870 grams.

The absence of a foot makes the reading slightly higher. The difference increases as the number of plies is increased, due to the additional air spaces between the plies, so when several piles are used the test without foot can be very inaccurate.

The errors arising in case (3) above are illustrated by experiments on test-pieces of various diameters and thicknesses under the following conditions:

- (1) with a foot 1.6 cm. diameter resting on the rubber under a load of 870 grams;
- (2) without the foot;
- (3) without the foot, and with the indenter resting on a 3 cm. diameter metal disc laid on top of the test-piece, so that the "indentation" reading was really the bodily compression of the rubber.

Results are given in Figure 1 as curves of the indentation (or compression in

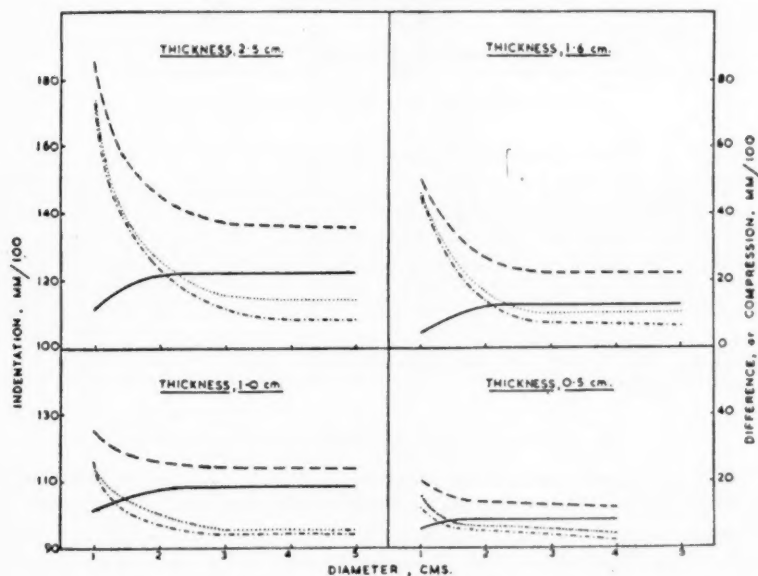


FIG. 1. ——— Indentation with foot. — — — Indentation without foot.
..... Difference due to foot. - - - - - Compression.

in test (3)) produced by increasing the load from 30 to 565 grams, plotted against diameter of the test-piece. The curves show that very high readings may be obtained without a foot when the diameter is small or, more precisely, when the ratio of diameter to thickness is of the order of unity or less. When a foot is used, small-diameter test-pieces tend to give low readings, for reasons not yet apparent, but the use of the foot clearly makes the reading less dependent on test-piece diameter. The difference between results with and without the foot approximately equals the compression in the test with a metal disc; although the agreement is not exact, it suffices to show that the unduly high readings obtained without the foot on small-diameter test-pieces are due to their being compressed bodily by the load.

The fact that even the largest-diameter test-pieces give different readings with and without the foot confirms other results¹ (Table 1), in showing that the use of a foot definitely reduces the indentation reading. To what extent this is due to elimination of the compression error and to what extent due to restriction of lateral deformations induced by penetration of the indenter is not yet clear.

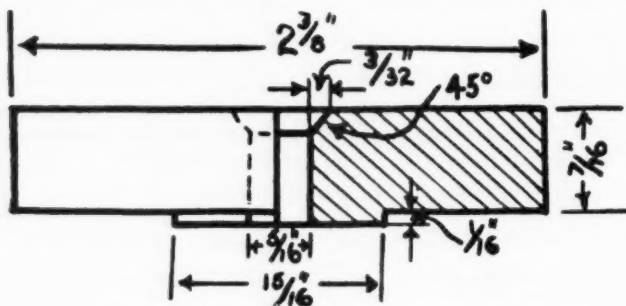


Fig. 2.—Circular lead weight for instruments without foot.

ERRORS IN PRESSER-FOOT METHOD

The use of a presser foot without a zero load gives inaccurate results if the upper surface of the rubber in the neighborhood of the indenter is not in contact with the foot while the indenting force is applied. This can happen, for instance, if the test-piece is (1) wedge shaped (see Figure 3); (2) thinner in the center than nearer the edges (Figure 4); (3) uneven on the upper surface (Figure 5); (4) in the case of very stiff rubbers, slightly curved (Figure 6). The error due to these causes is obvious and does not need experimental demonstration. (In Figures 3-6 the departure from ideal test-piece shape is, of course, exaggerated).

USE OF ZERO LOAD AND PRESSER FOOT TOGETHER

The use of both zero load and presser foot obviates many of the errors noted in the two preceding paragraphs, as the following considerations will show:

Elimination of errors that arise in using zero load alone (see section on "Errors in Zero Load Method" above).—In cases (1) and (2), i.e., where there is an air gap under or within the test-piece, the foot (provided it is smaller than the air gap and is pressed on to the rubber by a sufficient pressure) will more or less

FIG. 3.

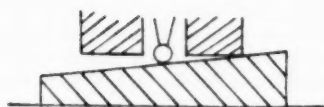


FIG. 4.



FIG. 5.



FIG. 6.



FIG. 7.

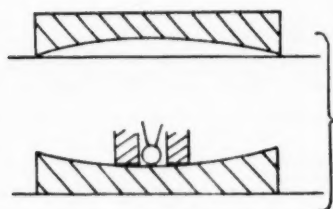
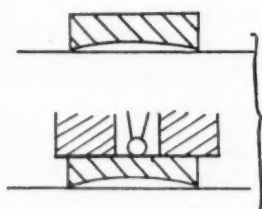


FIG. 8.



eliminate this gap and so lessen or avoid the bodily movement of the upper surface when the main load is applied (see Figure 7). However, if the foot is bigger than the air gap this advantage will not be obtained (see Figure 8).

To eliminate errors due to air gaps, it is not necessary to have a foot attached to the gauge; a loose annular weight (see Figure 2) resting on the test-piece will suffice. The following data for three stiff rubbers show how the use of such a weight can avoid the high results otherwise obtained on nominally flat parallel-faced test-pieces.

In case (3) (see section on "Errors in Zero Load Method" above), i.e., test-pieces of thickness equal to or greater than the lateral dimensions so that bodily

TABLE 2

EFFECT OF WEIGHT ON INDENTATION ² (MM./100)

(Mean of 6 readings on test-piece formed of 3 discs each 4 mm. thick;
loads: 30 and 565 grams)

	Without weight	With weight
Rubber I	62	54
Rubber II	55	43
Rubber III	62	34

compression occurs under the indenting load, the foot follows this compressive movement, which is thus not included in the measured indentation. Figure 1 shows how the use of the foot avoids the unduly high readings that are obtained on small-diameter specimens in absence of a foot. To eliminate this source of error, a foot attached to the gauge must be used; a loose weight is not sufficient, because application of the main indenting load still causes bodily compression of small-diameter specimens over and above any compression already produced by the weight.

Elimination of errors that arise in using presser foot alone (see section on "Errors in Presser-Foot Method" above).—Introduction of the zero load, to give a true zero position for the indentation measurement, avoids many of the errors that occur when the foot alone is used; this is evident from Figures 3-7. However, there are exceptions, as for instance the case illustrated by Figure 8; here the zero load is too small to eliminate the air gap under the test-piece, but the main load does so and thus depresses the top surface of the rubber.

The above considerations lead to the conclusion that the best form of hardness test should be that using both a presser foot and a zero load. Available data have, therefore, been studied to see whether they confirm this conclusion. In Table 3, Column (1) is the standard deviation among replicate measurements on the same test-piece (data from the experiments described in the section on

TABLE 3
STANDARD DEVIATION OF INDENTATION (MM./100)

(In Test 1, the indentation is that produced by 565 grams; in Tests 2-4 it is the difference between the indentations under 30 and 565 grams)

	(1)	(2)	(3)
Test 1: Without zero load; with foot	1.95	—	—
Test 2: With zero load; without foot; with weight*	1.3	2.0	3.4
Test 3: With zero load; without foot; without weight*	1.25	1.8	3.1
Test 4: With zero load; with foot	1.2	1.25	2.2

* Loose annular weight, as described above and shown in Figure 2.

"Vibration and Lubrication"; Tests 2 and 3 were made with an Admiralty type gauge³, and Tests 1 and 4 with an R.A.B.R.M. gauge⁴). Column (2) is the standard deviation of replicates, but all three forms of test were made with the new Wallace gauge fitted with a detachable foot⁵ (each figure is the mean for 12 rubbers); Column (3) is the variation (standard deviation) between mean results obtained in different laboratories (data from Table 7, averaging rubbers A-D, tests with lubrication).

All three sets of results show that the most reproducible readings are obtained by using both the zero load and the foot (Test 4); this advantage is particularly noticeable in Column (2), which is the more reliable because the comparison between the various forms of test is not interfered with by differences, *e.g.*, in amount of friction, between the instruments used.

PRESSURE ON FOOT

It is important to know whether the amount of pressure exerted by the foot on the rubber affects the test result. The following Table⁶ shows that varying this pressure over a considerable range does not appreciably alter the result when the indentation is measured as the difference between the readings under a zero load (30 grams) and a large main load (565 grams).

TABLE 4
EFFECT OF FOOT PRESSURE

Pressure on foot ($\frac{1}{4}$ inch diam.)	Indentation (mm./100)	Upward "bulge" of rubber due to increased pressure*
370 grams	82.9	—
1,100 grams	82.2	0.011 mm.
Heavy pressure applied by hand	82.5	0.049 mm.

* Measured at center of aperture in foot.

VIBRATION AND LUBRICATION

This section of the paper presents the results of an investigation to find whether vibration improves the uniformity of the readings and if any advantage accrues from the practice of lubricating the top surface of the rubber by dusting with talc.

Two types of hardness gauge were used; both were originally made to operate in accordance with B.S. 903-1940, and both fulfil the requirements of the 1950 issue except that the Admiralty gauge has no foot.

Admiralty gauge.—As this possesses no foot, the indentation is measured relative to the surface on which the rubber rests. The gauge stem plus indenter are made to weigh 30 grams (*i.e.*, the "zero" load) so that, by setting the gauge to read zero when the indenter is resting on the rubber, the reading obtained under the 565-gram load gives directly the differential indentation reading³. This gauge was used both with and without the weight described above and shown in Figure 2.

R.A.B.R.M. gauge.—The indentation is measured relative to a foot attached to the measuring gauge and resting on the rubber. The gauge is set to read zero when the tip of the indenter is in the plane of the foot; separate readings are taken under 30-gram and 565-gram loads, and the difference then taken⁴.

The tests, made on four rubbers (A, B, C, D), fall into two groups. *Group I*: Samples $2 \times 2 \times \frac{1}{2}$ inch of each rubber were distributed to seven laboratories, each of which made tests under the following conditions (4 readings under each condition):

- (1) no vibration; no lubrication
- (2) with vibration; no lubrication
- (3) no vibration; upper surface lubricated
- (4) with vibration; upper surface lubricated

Group II: Before the samples were distributed, Laboratory No. 1 made tests on all seven replicate samples of rubbers A, B, and C, using the Admiralty gauge (with and without weight); Laboratory No. 2 did the same with the Admiralty (with weight) and R.A.B.R.M. gauges. No lubrication was used in these tests.

The full results are given in the tables in the Appendix.

GROUP I RESULTS

Tables 5 and 6 give, respectively, the mean reading and the range among the four replicate readings for each test.

Effect of vibration on mean reading.—With the Admiralty gauge, vibration usually increases the reading slightly. The amount of this increase varies from one laboratory to another, and is negligible in Laboratories 3 and 6 but large in

2 and 4, especially when the test is made without the weight; thus, the average increases in Laboratory 2 are: without weight, 10; with weight, 3.4; in Laboratory 4: 4.6 and 2.5 respectively (all in mm./100); some tests on individual rubbers show even bigger effects (see Table 5). The grand mean effect of vibration, over all laboratories, instruments, and rubbers, is + 2.3 mm./100, which though small is statistically significant.

With the R.A.B.R.M. gauge, the effect of vibration varies even more, Laboratory 2 showing a decrease of 7.2 mm./100, and Laboratory 4 an increase of 5.6 mm./100. The overall average for the four laboratories (+ 0.3) is negligible, however.

Effect of lubrication on mean reading.—Although individual laboratories sometimes show a noticeable effect (e.g., Laboratory 2: increases of 4.0 and 2.1 mm./100 for Admiralty gauge without and with weight; Laboratory 4: increase of 3.6 with R.A.B.R.M. gauge), the effect is not consistent with any one type of instrument, and the grand mean effect is negligibly small. This result agrees with a previous investigation⁷, which showed that lubrication with talc scarcely affected the reading, although, on very thin test-pieces, lubrication with castor oil could have a large effect. There is, however, a variation between laboratories in the sense that in some, e.g., No. 3, the effect of lubrication is always negligible, whereas in others, e.g., Nos. 2 and 4, it is large and may be consistently in one direction (e.g., positive in Laboratory No. 2, Admiralty, with vibration; see complete data in Table 5). Comparison with the effects of vibration shows that the same laboratories obtain readings most (or least) affected by both vibration and lubrication; this suggests that the effects of both these factors are due largely to overcoming friction between the ball and the rubber surface, since lubrication of the latter would not affect friction in the measuring gauge; this point needs fuller investigation, however.

Effect of vibration on variation between laboratories.—Analyses of the complete data showed that the largest source of variance was usually the difference between laboratories, a result in line with that of many other studies of errors in rubber testing. It is, therefore, important to see whether vibration reduces these differences. Table 7 shows the variation between laboratory means.

Vibration usually reduced the spread between laboratories, especially when the spread without vibration was very large, as occurred particularly when using the Admiralty gauge without weight or the R.A.B.R.M. gauge.

From the smaller number of data obtained in the Group II results (Table 8) the effect of vibration in reducing between-laboratory variation does not appear significant except for rubber C.

Effect of lubrication on variation between laboratories.—Table 7 shows that lubricating the rubber surface usually helps to reduce excessive interlaboratory variation, thus acting similarly to, but less effectively than, vibration. It does not eliminate this variation, however, even when used in conjunction with vibration.

Effect of vibration on variation among replicate readings.—Study of the data for range of variation among replicates (Table 6) shows that vibration nearly always reduces this range, and in particular it avoids the very widely spread results sometimes obtained in the absence of vibration. Moreover, the greater uniformity produced by vibration is still apparent, and indeed highly significant, even when the rubber surface is lubricated with talc, so vibration is still advantageous even when lubrication is used.

Effect of lubrication on variation among replicate readings.—Examination of the replicate range figures in Table 6 shows that the main effect of lubrication

is to make the occurrence of excessive variation less frequent. There is thus definite evidence that uniformity of readings is improved by lubrication.

GROUP II RESULTS

Table 8 shows the effect of vibration on: (1) the mean hardness reading; (2) the range of variation among the four replicate readings on the same sample; (3) the range of variation among the 7 samples of the same rubber.

The test data were also examined by an analysis of variance in order to determine whether the observed effects of vibration and lubrication were large enough to be considered real or were merely the result of errors of measurement or other uncontrolled variation.

Table 8 shows that vibration sometimes increases and sometimes decreases the mean hardness reading, but the change is seldom greater than 2 or 3 units and is usually not significant relative to the variation between replicate readings. Because the effect of vibration varies from laboratory to laboratory and from rubber to rubber, the overall effect is not significant on rubbers A and B or on C with the Admiralty gauge; with the Laboratory 2 R.A.B.R.M. gauge vibration greatly reduced the mean reading on rubber C by eliminating the spuriously high readings in the region of 97 (a similar effect was found with rubber D in the Group I results, see Table 5).

Vibration considerably reduces the variation between replicate readings (column (2) of Table 8), as was found also in the Group I results.

The variation between samples (column 3 of Table 8) is significant with rubbers B and C, but not with A; on B and C the effect of vibration on the between-sample variation is not consistent enough to be significant.

The analyses of variance again show that the largest source of variation is that between "instruments".

CONCLUSIONS

In the light of the results and considerations discussed above, the British Standard hardness test was modified, in the 1950 issue of B.S. 903, by (1) stipulating the use of a foot in all tests on test-pieces with flat parallel faces, that is, other than small awkwardly shaped pieces like certain moldings; (2) requiring the test-piece surface to be dusted with talc. These two practices have been adopted also by the international rubber test methods Committee (ISO/TC/45), together with the use of the zero load and the practice of gently vibrating the instrument, which have always been specified in B.S. 903.

It has been noted above that the largest source of variation in hardness results is the lack of agreement between laboratories. It is not possible to say how much of this is due to the different instruments used and how much to the different operators. A perfect instrument should be independent of the operator, but experience shows that this ideal is difficult to achieve.

In the present investigation no special instructions were given as to adjustment or calibration of the instruments, and some unsuspected faults may have existed. In the R.A.B.R.M. gauge a source of error easily overlooked is incorrect balancing of the spring in the dial gauge; this leads to error⁸ mainly because it makes the zero load depart from the nominal 30 grams. This error would affect tests on all rubbers alike, but in the present investigation the inter-laboratory variations are not consistent among the four rubbers, so there must be other less obvious sources of error. With the Admiralty instrument, where the dial gauge spring is removed, zero-load errors should not arise; yet the

results still show a marked variation between instruments, and here the differences are found more consistently on all the rubbers.

Thus, although great improvements have been made in the accuracy of hardness testing as a result of this and previous investigations⁹, perfection has not yet been attained, and there is still scope for further study.

SUMMARY

Most hardness tests depend on penetration by an indenter under load, the penetration being measured by the movement of the plunger carrying the indenter. This movement must be measured from a zero position, and the fixing of this position has been the cause of most of the difficulties in obtaining accurate hardness measurements. In most instruments one of the following devices has been adopted: (1) *Zero Load*—a known small load is applied to the indenter, and its position under this load is taken as the zero; or (2) *presser foot*—an annular foot, surrounding the indenter, rests on the rubber test-piece, and the depth of indentation is measured relative to the plane of this foot.

Rubber test-pieces generally are not perfectly flat and parallel-sided, even though nominally so. This fact leads to errors in hardness measurements by instruments using either of the devices (1) or (2) mentioned above. Moreover, if plied-up test-pieces are used to obtain the required thickness, or in testing articles that are very thick compared with their lateral dimensions, large errors can arise if no foot is used. The best general procedure is, therefore, to use both a zero load and a presser foot. Experimental data support this conclusion, which has been embodied in the revised British Standard Method (B.S. 903-1950) and in the recommendations of Committee ISO/TC/45—Rubber.

Most published standard hardness tests make no provision for avoiding errors due to friction in the measuring device (usually a dial micrometer gauge). Results of tests show that by applying gentle vibration during the test, much more consistent readings are obtained, and it is possible to get better agreement between different laboratories and instruments.

Lubrication of the surface of the test-piece with talc produces a definite though small further improvement in uniformity of results. It is, therefore, a useful additional precaution.

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APPENDIX

In the tabulated results the following abbreviations are used:

- NV = no vibration.
V = with vibration.
NL = no lubrication.
L = with lubrication.
NW = no weight (Admiralty gauge).
W = with weight (Admiralty gauge).

TABLE 5
MEAN READINGS, GROUP I RESULTS

Gauge	Laboratory	Rubber A				Rubber B				Rubber C				Rubber D			
		NW		W		NW		W		NW		W		NW		W	
		NL	L	NL	L	NL	L	NL	L	NL	L	NL	L	NL	L	NL	L
Admiralty	1 NV	102	104	102	99	169	159	152	151	80	76	72	74	19	20	19	20
	V	106	106	101	102	162	161	152	154	78	77	75	77	21	21	20	20
	2 NV	98	103	98	102	126	138	150	145	68	70	70	68	11	14	14	20
	V	101	105	102	102	152	155	146	154	75	74	70	74	22	26	22	24
	3 NV	103	103	101	100	155	156	150	151	76	76	74	74	28	28	27	27
	V	103	103	101	100	155	156	151	152	76	77	75	74	28	28	28	27
	NV	103	108	109	108	158	153	158	158	84	80	78	69	24	21	22	26
	V	111	111	109	110	162	166	160	165	83	80	78	76	28	27	24	26
	4 NV	108	106	102	104	159	156	158	154	74	77	74	71	26	26	24	26
	V	106	105	103	102	159	161	158	156	75	78	73	73	24	26	25	24
	6 NV	110	109	107	109	160	156	154	158	76	73	71	76	23	22	24	21
	V	112	113	108	111	160	160	161	157	76	77	76	76	29	23	22	22
R.A.B.R.M.		NL		L		NL		L		NL		L		NL		L	
	2 NV	110(a)		114(b)		155		155		86		89		44		32	
	V	107		106		158		155		79		77		25		22	
	4 NV	102		110		140(c)		152		68		66		22		24	
	V	106		106		154		160		74		78		26		25	
	5 NV	99		102		158		157		76		76		26		26	
	V	104		104		162		162		78		77		26		25	
	7 NV	105		107		153		158		71		73		20		19	
	V	106		106		155		157		74		72		21		19	

Notes: (a) includes abnormal reading of 130.
(b) includes abnormal reading of 134.
(c) includes abnormal reading of 168.

TABLE 6
RANGE OF VARIATION AMONG 4 REPLICATE READINGS. GROUP I RESULTS
Figures in brackets are exclusive of the abnormal values noted in Table 5

Gauge	Laboratory	Rubber A				Rubber B				Rubber C				Rubber D			
		NW		W		NW		W		NW		W		NW		W	
		NL	L	NL	L	NL	L	NL	L	NL	L	NL	L	NL	L	NL	L
Admiralty	1 NV	12	1	1	2	2	3	2	8	2	2	2	1	1	1	1	1
	V	6	3	2	2	6	3	8	4	1	1	3	1	1	2	1	0
	2 NV	16	8	10	10	19	22	29	10	8	5	8	7	2	2	2	3
	V	4	8	2	2	5	4	8	4	4	5	3	7	3	2	1	3
	3 NV	3	0	1	1	2	3	3	2	2	3	2	3	3	1	1	2
	V	1	1	1	2	1	2	0	2	1	2	1	2	0	1	1	0
	4 NV	12	6	4	2	13	3	4	4	1	1	3	1	1	3	2	3
	V	1	2	1	3	1	2	1	1	4	0	3	3	1	1	1	1
	6 NV	3	4	6	1	6	8	4	4	2	6	3	2	0	1	1	1
	V	1	2	5	3	2	2	1	4	2	3	2	4	1	1	1	1
	7 NV	2	8	10	5	8	4	11	6	3	2	2	1	2	4	1	2
	V	4	1	1	4	5	4	5	6	2	3	5	2	4	3	1	4
R.A.B.R.M.		NL		L		NL		L		NL		L		NL		L	
	2 NV	26(1)		28(4)		7		5		20		18		13		21	
	V	1		2		3		1		2		2		3		1	
	4 NV	7		6		35(15)		18		21		7		2		3	
	V	2		2		3		2		4		3		0		2	
	5 NV	7		5		7		3		6		6		4		0	
	V	4		3		1		3		5		3		4		2	
	7 NV	2		4		4		1		0		5		1		2	
	V	1		1		6		2		3		1		2		2	

TABLE 7
VARIATION BETWEEN LABORATORIES EXPRESSED AS STANDARD DEVIATION
OF INDENTATION (MM./100)

Rubber		Admiralty gauge				R.A.B.R.M. gauge*	
		No weight		With weight		NL	L
		NL	L	NL	L		
A	NV	4.3	2.6	4.1	4.1	4.7(2.5)	5.0(3.3)
	V	4.3	3.9	3.6	4.7	1.3	1.0
B	NV	14.8	5.4	3.7	5.0	8.1(12.3)	2.7
	V	4.0	4.0	5.9	4.6	3.6	3.1
C	NV	5.5	3.5	2.9	3.2	7.9	9.6
	V	3.1	2.0	2.7	1.6	2.6	2.7
D	NV	6.1	4.9	4.6	3.3	8.5	4.2
	V	3.5	2.6	2.8	2.6	1.8	2.2

* Figures in brackets are exclusive of the abnormal readings noted in Table 5.

TABLE 8
EFFECTS OF VIBRATION OF MEAN READING, RANGE OF 4 REPLICATE READINGS,
AND RANGE OF 7 SAMPLES (ALL FIGURES IN MM./100)

Laboratory and instrument		(1) Mean			(2) Weplicate range (a)			(2) Sample range		
		A	B	C	A	B	C	A	B	C
1. Admiralty, no weight	NV	103.6	164.5	77.3	6.3	6.4	3.0	6	6	8
	V	108.4	167.1	75.5	3.3	4.7	3.0	2	8	9
1. Admiralty, with weight	NV	101.7	152.8	71.0	2.9	5.0	2.6	2.5	4	7
	V	100.2	152.7	72.7	3.0	3.9	2.0	1.5	4	7
2. Admiralty, with weight	NV	100.0	145.4*	65.5	11.1	12.4	6.1	7.5	6	11
	V	100.1	146.7	68.1	3.9	6.4	4.3	5	3	7
2. R.A.B.R.M.	NV	104.5†	156.2‡	85(b)	3.3	4.3	22.0	3	2	?
	V	106.1	156.1	75.2	2.0	1.7	3.4	2.5	2	7

Notes: (a) mean of ranges for the 7 samples. (b) individual readings ranged from 74 to 113, but were mostly grouped around 77 or 97.

* Excluding one reading of 168 (inclusive mean = 146.2).

† Excluding two readings of 130 and 132 (inclusive mean = 106.4).

‡ Excluding two readings of 175 and 199 (inclusive mean = 158.4).

TEMPERATURE RISE IN THE RUBBER IN ROTATION PLASTOMETERS *

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INTRODUCTION

One of the limiting factors that prevent the use of rotation plastometers for measuring the rheological properties of unvulcanized rubber at rates of shear as high as those met in processing has been the excessive temperature rise, due to the energy dissipated in the rubber during shearing. The magnitude of this rise has been estimated on theoretical grounds¹, but apparently has not previously been measured.

The following theoretical expressions are readily derived for an infinite plane sheet of rubber confined between parallel surfaces at a constant temperature and sheared at a uniform rate, flow being in laminae parallel to the surfaces:

$$T = SMa^2/3KJ \quad (1)$$

$$t = a^2H/6K \text{ approx.} \quad (2)$$

Here T is the mean excess temperature of the rubber above the surface temperature ($^{\circ}\text{C}$) under steady state conditions, and t is the period of shearing (sec.) required for the mean temperature of the rubber to rise by $\frac{1}{3}T$ on commencing shearing. S is the shear stress (dyne. cm.^{-2}), M the strain rate (sec.^{-1}), $2a$ the thickness of the rubber (cm.), K the thermal conductivity of the rubber (C.G.S. units), J is Joule's Equivalent, and H the specific heat of rubber ($\text{cal.g.}^{-1} \text{ } ^{\circ}\text{C}^{-1}$).

These equations would be expected to apply fairly accurately to concentric-cylinder plastometers. Application to the shearing cone plastometer² assumes that temperature gradients in directions parallel to the confining surfaces are small compared with the gradient perpendicular to the surfaces, and that excess heat is readily dissipated from the rotor, which is probably not true.

Two experimental techniques to check these equations are described below. All measurements were made in the shearing cone modification² on Mooney's shearing disc plastometer³.

THERMOCOUPLE MEASUREMENTS

The following design of thermocouple was considered to be the most satisfactory compromise, being strong enough to withstand the force exerted by the rubber without providing a highly conducting path which would carry the heat away from the thermojunction. An enamelled copper wire was passed down a hypodermic needle, 0.022 inch outside diameter, and soldered to the tip of the needle. The needle was mounted in a steel tube, 0.11 inch internal diameter, the needle being located by glass beads, but otherwise air-insulated. This as-

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ssembly replaced one of the plungers used to keep the rubber under pressure. All results have been converted to degrees C relative to the upper platen, as a preliminary experiment with the rotor stationary showed that the thermocouple temperature followed the upper platen temperature. Owing to the high thermal conductivity of the needle, the temperature indication with the needle inserted to the center of the rubber would be expected to be controlled by the mean temperature of the rubber rather than the maximum temperature at the center of its thickness.

In these experiments, the rubbers used were lightly masticated smoked sheet, and an MPC black master batch (50 parts black to 100 rubber). The rubber was sheared alternately at rates 1.0 and 10.0 sec.⁻¹, since it was shown by a preliminary experiment that shearing at 1.0 sec.⁻¹ caused no detectable rise in temperature. The measured and theoretical temperature rises are given in Table 1. There is uncertainty as to the value of some of the factors in Equation 1, particularly for the thermal conductivity, as various authors⁴ differ on the actual value and its dependence on temperature. The values used here were 4.0×10^{-4} and 6.0×10^{-4} (c.g.s. units) for the smoked sheet and black stock, respectively. The thickness of the rubber was taken as 0.37 cm., assuming the plane midway between the tops and bottoms of the serrations to be the plane of contact.

TABLE 1
MEASURED AND CALCULATED VALUES OF MEAN TEMPERATURE RISE

Material	Shear stress at 10 sec. ⁻¹	Temperature rise (°C)	
		Measured	Calculated
Masticated smoked sheet	1.60×10^8 dynes/cm. ²	5.5	11
MPC black master batch	1.12×10^8 dynes/cm. ²	3.2	5

The results in Table 1 suggest that the thermocouple technique is unsatisfactory for determining the actual temperature rise, presumably because of conduction of heat away from the tip of the needle. However, these experiments showed that the time taken to reach a temperature rise one-third of the maximum is 30–45 seconds for smoked sheet, as compared with the theoretical value of about 7 seconds. Tests using the thermocouple flush with, but thermally insulated from, the upper platen surface show no temperature increase on shearing the rubber. Thus as the rubber immediately in contact with the platen surface does not change in temperature, the most probable explanation of this time discrepancy is that the rotor heats up. Estimates of the heat capacity of the rotor show that the time taken for the rotor temperature to rise 5° C would be 30–60 seconds, using the masticated smoked sheet, a result in general agreement with the experimental times. Owing to the complication of the system, particularly the unknown rate of heat loss from the rotor, it is not possible to calculate the temperature rise to be anticipated in the rubber as the rotor heats up, but the value given by the original theoretical equation might be expected to be increased by a factor of about 2. An alternative experimental approach to the problem is described in the next section.

SCORCH TESTS

It has been found that the rate of scorching of a mix in the shearing cone plastometer is increased by shearing at a high rate. The possible explanations

are that the stirring action increases the reaction rate, or that there is a considerable temperature rise. In the following experiments an attempt was made to eliminate the first possibility by the use of accelerators having different temperature coefficients of activity. If, as in fact was found, there is general agreement between the estimates of temperature rise for the two stocks, the probability that the stirring action would increase the reaction rate in the ratio of the temperature sensitivities is slight, so that it may be taken as reasonably established that the temperature increase is the predominant influence.

The procedure followed was to carry out normal scorch tests on each material at 100°, 110°, and 120° C, at a shear rate of 1.0 sec.⁻¹, shearing commencing 1 minute after closing the mold, to assess the temperature coefficient of the reaction. This test was followed by a 100° C test on a new sample of the stock at a shear rate of 10 sec.⁻¹. After a period at this rate, the stock was sheared at 1.0 sec.⁻¹ to obtain a scorching curve which, by comparison with the previously obtained 100° C curve, indicated the extent of the heating produced by the 10 sec.⁻¹ shearing.

The "pure-gum" mixings used had the following composition (parts by weight): smoked sheet 100, zinc oxide 5, stearic acid 1, sulfur 2, accelerator 0.375. The accelerators used were tetramethylthiuram disulfide, and a delayed-action type with a high temperature coefficient of activity. A further

TABLE 2
TEMPERATURE RISE FROM SCORCH TESTS

Type of stock	Temperature rise in degrees C		Experimental
	Experimental	Theoretical	
Pure gum (tetramethylthiuram disulfide)	12	5.4	2.2
Pure gum (delayed-action accelerator)	10	5.4	1.9
Tread type	14	7.3	1.9

test on a black-loaded tread type stock was less satisfactory, as the rapid shearing softened the stock, and subsequent curves at 1.0 sec.⁻¹ were not directly comparable with curves obtained by shearing throughout at the lower rate. Table 2 gives the temperature rise determined in this way for the three stocks, together with the value calculated from the original theoretical equation.

The theoretical value assumes that the whole of the rubber has the same mean temperature as the thickest part, and should therefore be an overestimate of the mean temperature. The measured values are, however, greater than those calculated, by a factor of about 2, which is consistent with the assumption above that the rotor heats up.

DISCUSSION

In the rotating cylinder instruments of Mooney¹ and of Hamm and van Rossem⁵, the temperatures of rotor and stator were controlled independently, so that the original temperature rise expression would be expected to apply. As has been pointed out previously⁶, some of Mooney's results are to be suspected because of the likelihood of an excessive temperature rise. The shear rates used by Hamm and van Rossem were sufficiently low to avoid this trouble.

Although the rate of shear in the Mooney shearing disc plastometer, *i.e.*, using the original type of rotor, is considerably lower than the rate considered in the experimental results above, the rubber in the edge zone is in a thick layer.

Consequently, using an extremely stiff rubber (Mooney value, with large rotor, 200) a temperature rise, at least locally, of 10°C is possible. However, mixed stocks for scorch tests are normally much softer than this and in any case, as this instrument is always used at the same speed, relative plasticity or scorch values in comparing stocks of not very different stiffness, *e.g.*, in control tests or repeat batches, will not be appreciably affected.

SUMMARY

The temperature rise that occurs on shearing rubber at high rates in the shearing-cone plastometer has been measured and shown to be about double that which is to be expected from simple theoretical considerations. This discrepancy is apparently due to heating of the rotor. The temperature rise in normal Mooney plastometer tests may be great enough to influence significantly the results, particularly during scorch tests, but relative results on stocks of not very different plasticities (as in control tests of a given mix) would not be appreciably affected.

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EFFECT OF SPEED OF STRIPPING ON THE MEASURED ADHESION BETWEEN CONVEYOR-BELTING PLIES *

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INTRODUCTION

No work seems to have been published on the effect of stripping speeds on the determination of adhesion of conveyor-belted plies. It seemed desirable to make a preliminary study to indicate the order of any observable variations and to place on record the results obtained for the guidance of those engaged in drawing up specifications.

GENERAL EXPERIMENTAL PROCEDURE

For the first series of tests, the specimens, 1 inch wide and approximately 7 inches long, were cut longitudinally from a sample of belting. The rubber covers and each ply were separated for a distance of $1\frac{1}{2}$ inches. The thicker rubber cover, *i.e.*, on the carrying face of the belting, was stripped first in each case and is designated "top rubber" in the results. Each consecutive ply was then stripped down to the "bottom rubber", *i.e.*, the rubber cover on the pulley face of the belt; thus six series of stripping loads were obtained with each strip. It was found to be more convenient to carry out the stripping in this way rather than according to B.S. 490.

The stripping was carried out with a range of constant speeds. Preliminary experiments were carried out on a Hounsfield tensometer mechanized with a d.c. motor. Unfortunately the automatic load-recording mechanism for this machine was not available at the time, and it was necessary to take readings visually from the mercury gauge. This was found to be unsatisfactory because the load variations were too great to make accurate estimates of the load as stripping proceeded. A few results are, however, given for a range of speeds for the top rubber and second ply adhesion strengths (see Table 2).

The greater part of the work was continued on a Schopper tension testing machine modified with suitable pulleys to give a range of speeds. Loads were recorded autographically, and two separate test-pieces were used for each speed. Ten readings were taken from the chart for each ply separation and the mean stripping load calculated (see Table 1).

During the stripping process it can be seen that a line of rubber strings (formed by the penetration of the rubber through the interstices of the fabric) gradually builds up and the load increases at the same time; as these strings break, the load falls and increases again as the next line builds up. With a higher rate of stripping, the building up of consecutive lines of rubber strings proceeds at a faster rate, and when one line breaks down the next is building up immediately and the load remains almost constant. It was thought at first

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that this might lead to more uniform load reading at higher rates of stripping, but the gain could not be assessed in this first series of experiments since, although more uniform loads were recorded, it was realized that this might be due to the apparatus used being fitted with a dashpot which provided some damping; the second series of tests showed this to have been the case.

The second series of tests were carried out on specimens kindly supplied by the Dunlop Rubber Co., Ltd. The belting as supplied was already cut into strips 1 inch wide. Both rubber layers appeared to be of the same thickness and it was, therefore, impossible to distinguish pulley and carrying sides of belt. All strips had sample numbers or something similar on one side and for convenience this was called the "top" rubber; the succeeding plies were numbered 1 to 4 and lastly the "bottom" rubber.

All stripping was carried out on the Hounsfield tensometer, the automatic load-recording mechanism mentioned above being now in good working order. Rates of 1 and 5½ inches per minute were obtained by hand driving of the machine and higher rates mechanically. The speeds given are actually those recorded electrically during the stripping process and not the nominal rate (calibrated without load). Specimens 6 inches long were used, but it should be noted that when testing the rubber layers on the top and bottom of the belt, elongation of the rubber was fairly large and only about 3 inches could be stripped because of the short run available with this machine. Loads were recorded autographically and ten readings were taken for each strip (see Table 3).

Loads were rather variable, as reported for the first series, and it is of interest to note that this condition did not improve with the higher rates of stripping, confirming that the high inertia of the Schopper machine was responsible for the smoothing out of the load/distance curves with increasing rate of stripping.

Two strips were used for stripping as before, *i.e.*, stripping from top to bottom rubber. Two other strips were used for testing the last three plies only. Thus, two sets of results were obtained, the method of the first corresponding to that of the first series and that of the second corresponding to the procedure laid down in B.S. 490. The procedure for the top rubber and first two plies was, of course, the same for both and was not, therefore, repeated.

RESULTS

FIRST SERIES

TABLE I
RESULTS OBTAINED WITH A SCHOPPER TENSION TESTING MACHINE

Rate of stripping (in./min.)	Load in pounds					
	Top rubber	1st ply	2nd ply	3rd ply	4th ply	Bottom rubber
1	24.0	28.0	23.8	27.5	20.0	19.6
	22.7	26.0	23.3	26.2	19.6	20.5
5.25	24.2	26.2	24.7	27.7	22.2	23.8
	26.9	25.5	25.5	27.1	22.7	25.5
11	26.7	26.7	24.4	28.9	22.0	25.3
	25.8	30.6	26.7	28.6	23.6	27.1
38.8	27.1	26.7	24.4	29.5	25.3	26.2
	26.7	26.7	24.9	27.1	22.9	27.1

TABLE 2
RESULTS WITH A HOUNSFIELD TENSOMETER

Mean rate of stripping (in./min.)	Load in pounds	
	Top rubber	Second ply
12.4	22	18*
	26	28
21.8	29	28
	31	27
65.3	28	28
	28	30

* Omitted in calculation.

SECOND SERIES

TABLE 3
RESULTS OBTAINED WITH MODIFIED HOUNSFIELD TENSOMETER

Rate of stripping (in./min.)	Load in pounds								
	Tested according to B.S. 490						Tested in order		
	Top rubber	1st ply	2nd ply	3rd ply	4th ply	Bottom rubber	3rd ply	4th ply	Bottom rubber
1	23.8	30.2	28.6	30.1	28.4	24.4	29.7	27.7	22.4
5.5	25.7	32.8	31.1	30.3	32.0	25.8	31.6	28.9	24.1
13	26.3	31.9	30.7	30.8	30.9	26.4	29.9	29.4	25.3
24	26.2	32.7	31.4	31.3	31.8	26.8	32.1	30.9	24.8
49	26.8	33.1	31.2	30.9	31.9	27.6	33.2	28.6	25.4
74	28.1	35.2	33.0	30.6	33.2	27.9	31.0	30.8	27.2

TABLE 4
EFFECT OF RATE OF STRIPPING ON LOAD

Experiment	Ply	Regression equation	Standard deviation (lb.)
1st series	Top rubber	$y = 2.74x + 23.3$	1.9
	1	Not significant	1.6
	2	$y = 2.26x + 23.6$	1.6
	3	Not significant	1.1
	4	$y = 2.05x + 20.8$	1.1
	Bottom rubber	$y = 4.29x + 20.8$	1.3
2nd series	Top rubber	$y = 1.96x + 23.9$	0.5
	1	$y = 2.08x + 30.3$	0.9
	2	$y = 1.83x + 28.9$	0.7
	3	Not significant	1.2
	4	Not significant	1.3
	Bottom rubber	$y = 2.15x + 22.4$	0.6
	3	Not significant	0.45
	4	$y = 2.13x + 28.95$	0.8
	Bottom rubber	$y + 1.86x = 24.4$	0.07

(a) Tested in order.

(b) Tested in accordance with B.S. 490.

The loads recorded suggest a straight line when plotted against the logarithm of the rate of stripping, and for this reason a regression line has been calculated, where it is shown to be significant at the 5 per cent level. The significance of the regression line was determined by analysis of variance, the variance due to the line being compared with the residual variance about the line. This residual variance is used for calculating the standard deviation of the load determination when the regression is significant, and where it is not, the total variance has been used. The analytical results are shown in Table 4, in which y = the load recorded in pounds and $x = \log_{10}$ (rate of stripping in inches per minute).

DISCUSSION OF THE RESULTS

The size of the standard deviation shows that, although for a majority of plies the load is demonstrably dependent on the rate of stripping, the dependence can be ignored over a fair range of rates. The accuracy of experimentation

TABLE 5
SEPARATION LOADS AT 1 INCH PER MINUTE

Experiment	Ply	Load (lb.)	Standard deviation (lb.)
1st series	Top rubber	23.3	1.9
	1	26.7	1.6
	2	23.5	1.6
	3	26.7	1.1
	4	20.8	1.1
	Bottom rubber	20.8	1.3
2nd series	Top rubber	23.9	0.5
	1	30.3	0.9
	2	28.9	0.7
	3	31.3	1.2
	4	29.4	1.3
	Bottom rubber	22.4	6.6
	3	30.6	0.45
	4	29.0	0.8
	Bottom rubber	24.4	0.07

(a) Tested in order.

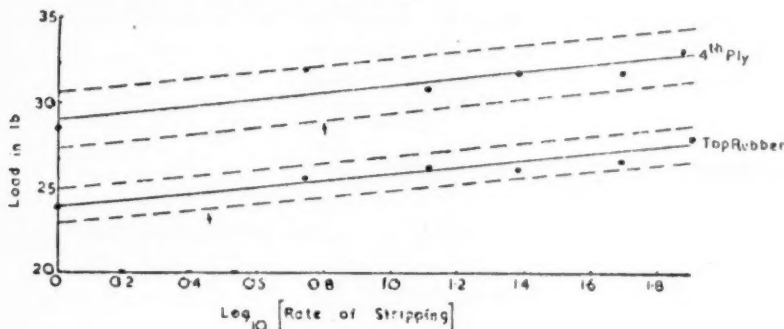
(b) Tested in accordance with B.S. 490.

seems better in the second series than in the first, but it may be remarked that this was achieved only by means outside the scope of most testing laboratories. The load was continuously recorded by a mechanical engine indicator, and electrical means were adopted for marking on the same record the time and space. The following remarks apply to the second series of results. The significance of the regression was naturally greatest where the variance about the regression line was least, and for this reason the regression coefficients for the top and bottom rubbers (tested as B.S. 490) were compared. They are not significantly different. The same finding applies also to the highest and lowest regression coefficients, 2.15 and 1.83; they are not demonstrably different. It follows, therefore, that it cannot be shown from the present data that the influence of rate of stripping on the separation load for different plies is different. This does not mean that the separation load for the different plies is the same, and reference to Table 5 shows that the separation loads for a stripping rate of 1 inch per minute are significantly different in some cases. The appropriate

figure for separation load at 1 inch per minute is obtained by putting $x = 0$ in the regression equation or, if the regression is not significant, by taking the mean for all rates of stripping.

Considering only the second series, we find the separation loads differ significantly between the facing rubbers, *i.e.*, both top and bottom, and the numbered plies, but not between the numbered plies themselves. There are no differences between stripping in order or stripping in accordance with B.S. 490 for the numbered plies, but the results obtained by the two different methods are different for the bottom rubbers. The top and bottom rubbers are indistinguishable in both cases.

The figure shows the calculated regression lines for the top rubber and 4th ply of the second series tested in accordance with B.S. 590, together with the actual experimental points. The broken lines are added at $\pm 2\sigma$ to illustrate the fiducial limits. The difference in the level will be easily noticed, together with the indistinguishability of the slopes of the lines, even though the regression coefficients are 1.96 and 2.13, respectively.



CONCLUSIONS

Ply adhesion depends on the rate of stripping, but this dependence is small compared with the experimental error.

In the belting examined in the second series of experiments the observed standard deviation is, on average, 0.7 pound. If, conveniently, twice the standard deviation is taken as the permissible variation, then with the observed regression equations of $y = 2.0x + C$, a rate of stripping of 5 inches per minute is required on one side of the specification rate of 1 inch per minute and, assuming the validity of extrapolation below the lowest rate actually realized, 0.2 inch per minute on the other side. These limits will, of course, vary with the belting samples, but they are indicative of the relative insensitivity of the load to the rate of stripping. For the first series of results given here, the corresponding figures give much wider limits.

The sensitivity to rate of stripping seems to be the same for all plies.

SUMMARY

No work seems to have been published on the effect of stripping speeds on the load required to separate belting plies. This report is a preliminary study to indicate the order of any effects. Two series of tests were carried out, with stripping rates of 1 inch per minute up to 74 inches per minute. Statistical ex-

amination of the results shows that the measured ply adhesion depends on the rate of stripping, and can be regarded as a linear function of the logarithm of the rate. The experimental error in determining ply adhesion is, however, relatively large, and in the second series of experiments the standard deviation was just under 1 pound per inch of width. It follows from this that for a specification rate of stripping of 1 inch per minute no significant difference would, in fact, be found if the rate dropped as low as 0.2 inch per minute or rose to 5 inches per minute. The report should be of interest to those engaged in fixing limits for specification tests.

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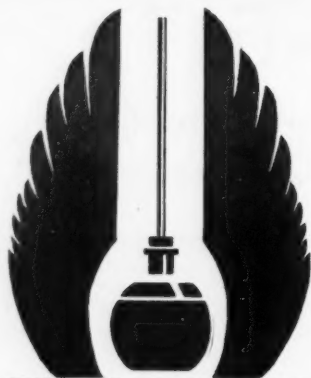
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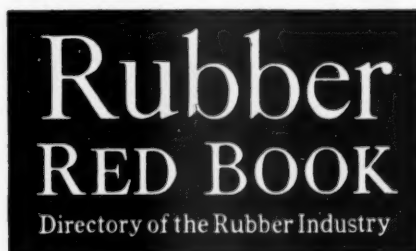


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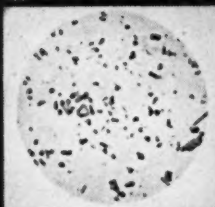
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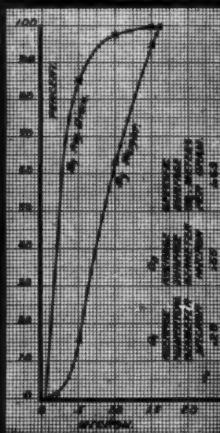
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